UNLV | University Libraries
University of Nevada, Las Vegas

UNLV Theses, Dissertations, Professional Papers, and Capstones

8-1-2015

Versatile Synthetic Methods for Photoluminescent Pyrylium Tosylates

Jung Jae Koh
University of Nevada, Las Vegas, kohj@unlv.nevada.edu

Follow this and additional works at: https://digitalscholarship.unlv.edu/thesesdissertations

 Part of the Chemistry Commons

Repository Citation
Koh, Jung Jae, "Versatile Synthetic Methods for Photoluminescent Pyrylium Tosylates" (2015). *UNLV Theses, Dissertations, Professional Papers, and Capstones*. 2487.
https://digitalscholarship.unlv.edu/thesesdissertations/2487

This Thesis is brought to you for free and open access by Digital Scholarship@UNLV. It has been accepted for inclusion in UNLV Theses, Dissertations, Professional Papers, and Capstones by an authorized administrator of Digital Scholarship@UNLV. For more information, please contact digitalscholarship@unlv.edu.

VERSATILE SYNTHETIC METHODS FOR PHOTOLUMINESCENT PYRYLIUM TOSYLATES

by

Jung Jae Koh

Bachelor of Biochemistry
University of Nevada, Las Vegas
2011

A thesis submitted in partial fulfillment
of the requirements for the

Master of Science - Chemistry

Department of Chemistry and Biochemistry
College of Science
The Graduate College

University of Nevada, Las Vegas
August 2015

Copyright by Jung Jae Koh, 2015

All Rights Reserved

UNLV | GRADUATE COLLEGE

Thesis Approval

The Graduate College
The University of Nevada, Las Vegas

July 21, 2015

This thesis prepared by

Jung Jae Koh

entitled

Versatile Synthetic Methods for Photoluminescent Pyrylium Tosylates

is approved in partial fulfillment of the requirements for the degree of

Master of Science – Chemistry
Department of Chemistry and Biochemistry

Pradip K. Bhowmik, Ph.D.
Examination Committee Co-Chair

Kathryn Hausbeck Korgan, Ph.D.
Graduate College Interim Dean

Vernon F. Hodge, Ph.D.
Examination Committee Co-Chair

Dong-Chan Lee, Ph.D.
Examination Committee Member

Laxmi P. Gewali, Ph.D.
Examination Committee Member

Anjala Krishen, Ph.D.
Graduate College Faculty Representative

ABSTRACT

Versatile Synthetic Methods for Photoluminescent Pyrylium Tosylates

by

Jung Jae Koh

Dr. Pradip K. Bhowmik, Examination Committee Chair
Department of Chemistry and Biochemistry
University of Nevada, Las Vegas

Pyrylium salts are an important class of cationic organic molecules that exhibit good absorption, fluorescence, and photo-induced electron transfer properties. They can also function as precursors for synthesis of different heterocyclic organic molecules such as furan, pyridine, pyridinium salt, and betaine dyes. This thesis describes versatile methods of synthesis for a series of 2,4,6-triarylsubstitued pyrylium tosylates with different substituents by using *p*-toluenesulfonic acid monohydrate instead of conventional acid catalysts including perchloric acid or boron trifluoride diethyl etherate that accompany explosion danger and difficult storage problem, respectively. The chemical structures were established by ^{1}H and ^{13}C NMR spectroscopic techniques and elemental analysis, and their thermal properties were studied by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC). Their optical properties including quantum efficiency were measured by UV-Vis and photoluminescent spectroscopy, and they emitted blue and green color depending on the substituents in 2- and 6-positions of phenyl groups.

ACKNOWLEDGMENTS

First and foremost I would like to express my sincere gratitude to my advisor Dr. Pradip K. Bhowmik, who has supported me throughout my thesis with his continuous support, guidance, patience, motivation, enthusiasm, and immense knowledge. I would also like to express deep appreciation for my committee members, Drs. Vernon Hodge, Dong-Chan Lee, and Laxmi Gewali, for their time, encouragement, insightful comments, and suggestions to improve my thesis. I would like to thank Dr. Haesook Han for her immense advices and assistance in the lab.

I am thankful to the Chemistry Department's faculty and staff members, especially, Dr. Dennis Lindle, Dr. David Hatchett, Dr. Kathleen Robins, Dr. Jun Yong Kang, Dr. Balakrishnan Naduvalath, Mark Miyamoto, Deborah Maters, and Carolyn Hatchett, for the assistance and advices. In my daily work I have been blessed with a friendly and cheerful group of collegues (Dr. Tae Soo Jo, Dr. Van Vo, Dr. Alexi Nedeltchev, Ontida Tanthmanatham, Mihaela Ciulei, Rui Wang, Yongke Tan, Christy Lee, and Shane Killarney).

Finally, I would like to express my deepest gratitude to my family for supporting me immensely and spiritually: My parents Tae Hwan Koh and Gui Rye Lee, and my sister Ara Koh, I could not have imagined achieving the successful completion of my thesis without them.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SCHEMES

CHAPTER 1

INTRODUCTION

1.1. Background and Significance

Pyrylium cations are six-membered aromatic rings containing one positively charged oxygen heteroatom, which is the most electronegative element that can be a part of an aromatic system.[1] In general, pyrylium cations accompany non-nucleophilic anions such as tetrafluoroborate, perchlorate, hexafluorophosphate, hydrogensulfate, and trifluoromethanesulfonate (triflate).[2] The first pyrylium salt with perchlorate as the counterion was introduced in 1911 by Baeyer,[3] and initial interest in this type of compounds was moderate until early 1960s. However, the synthesis of pyrylium salts rapidly increased because they were recognized as important intermediates for the synthesis of various substituted furan, pyridine, and pyridinium derivatives.[4-6]

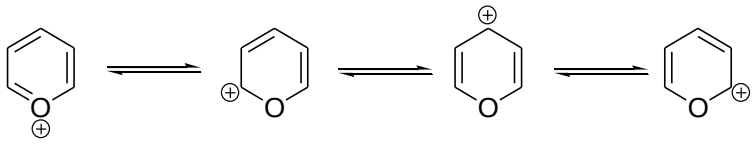


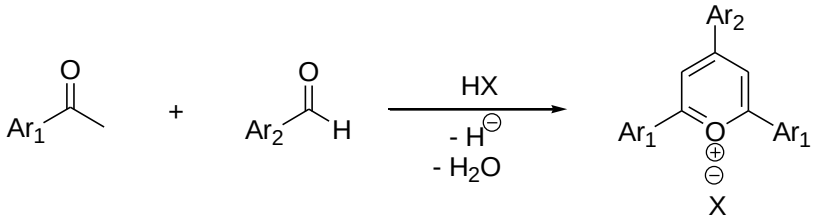
Figure 1. Resonance structures of the pyrylium cation.

The pyrylium ring is relatively stable and its stability can be explained by aromaticity. However, the aromatic stabilization of the pyrylium ring is low and its reactivity differs from other aromatic rings such as benzene or pyridine. As shown in Figure 1, the positive charge attached to the oxygen is delocalized over the whole ring. According to the resonance structures above, the positive charge is delocalized over the α-positions (2- and 6-positions) and γ-position

(4-position). The α-positions of the pyrylium ring can be easily opened by a nucleophilic attack because electron deficiency in the α-position is greater than the γ-position based on NMR spectroscopy and theoretical calculation studies.[2,7]

The synthesis of pyrylium salts is very attractive because pure form of pyrylium salts can be easily isolated from acyclic precursors without complicated separation procedures due to their ionic characteristics.[1] In general, salt-like character of pyrylium salts makes them insoluble in diethyl ether or hydrocarbon unless they have large hydrophobic groups, therefore, the starting materials and byproducts can be easily removed by simple washing with diethyl ether.[1,2] In contrast, the solubility of pyrylium salts is an essential factor that allows easy separation, and it is greatly affected by the nature of anions as well. In the initial work performed by Baeyer[3,8] and Dilthey,[9] perchloric acid was employed in the synthesis of pyrylium salts that leading the moderate solubility characteristics with the perchlorate anion, which is the reason for being the anion of choice at that time.[3,8,9] However, nowadays, because of the explosion danger, the perchlorate anion is replaced by other anions such as tetrafluoroborate, hexafluorophosphate, or triflate anions due to safety and their convenient solubility properties as perchlorate anions.[2] Among those anions mentioned above, hexafluorophosphate anion leads the solubility even lower than the other anions.[2] On the other hand, anions such as sulfoacetate, hydrogensulfate, halide, tetrachloroferrate, and picrate lead to higher solubility of the corresponding salts that often result difficult separation from reaction mixtures.[2] Especially, halide (bromide or chloride) anions in alkyl-substituted pyrylium salts result even hygroscopic property.[2] In addition, hydrogensulfate or sulfoacetate anions lead to the ease of synthesis because of the high yields and solubility, but acidic hydrogens may interfere in subsequent reactions, so that they need to be

Table 1. Reported synthesis of symmetrically substituted 2,4,6-triarylpyrylium salts from aryl methyl ketones and benzaldehydes



Ar_1	Ar_2	X	Conditions	Yield (%)	mp (°C)	Ref
Ph	Ph	ClO_4	$HClO_4$/toluene	49	273	12
Ph	Ph	ClO_4	1. H_2SO_4 2. $HClO_4$	NA	271	13
Ph	Ph	BF_4	$BF_3 \cdot OEt_2$	40	255	14
Ph	Ph	$FeCl_4$	$FeCl_3$/AcOH	49	277	9
4-Tol	Ph	BF_4	BF_3/AcOH	50	268-269	15
4-Tol	Ph	BF_4	$BF_3 \cdot OEt_2$	40	311	14
4-Tol	Ph	$FeCl_4$	$FeCl_3/Ac_2O$	25	278-280	16
4-BrC_6H_4	Ph	BF_4	$BF_3 \cdot OEt_2$	38	356	14
4-$MeOC_6H_4$	Ph	ClO_4	1. H_2SO_4 2. $HClO_4$	NA	274-275	13
4-$MeOC_6H_4$	Ph	ClO_4	1. $POCl_3$ 2. $HClO_4$	NA	NA	13
4-$MeOC_6H_4$	Ph	BF_4	BF_3/AcOH	31	NA	14
4-$O_2NC_6H_4$	Ph	BF_4	BF_3/AcOH	70	NA	15
4-ClC_6H_4	4-ClC_6H_4	BF_4	$BF_3 \cdot OEt_2$	40	309	14
4-Tol	4-Tol	$FeCl_4$	$FeCl_3/Ac_2O$	31	260	17
4-$MeOC_6H_4$	4-$MeOC_6H_4$	ClO_4	1. H_2SO_4 2. $HClO_4$	NA	256	13
4-$MeOC_6H_4$	4-$MeOC_6H_4$	ClO_4	1. $POCl_3$ 2. $HClO_4$	NA	NA	13

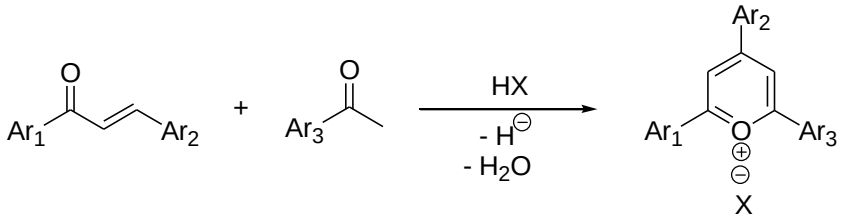
NA = Not Available.

exchanged to more adequate anions in order to obtain the pure product without any difficulty in isolation process.[2]

Substitution patterns in the pyrylium ring are very important for its chemical reactivity. Pyrylium salts become highly reactive and require strong acids to prevent hydrolysis when one or both α-positions are unsubstituted, and they become sensitive to moisture that resulting a fairly low yield.[2] In this case, water is strong enough to become attached to the α-position and opens the pyrylium ring, so that 2-hydroxypyran is yielded.[2] However, the presence of electron donating groups such as dialkylamino or aryl groups stabilize the pyrylium ring, so that its reactivity reduces significantly towards nucleophiles.[10] Especially, among various pyrylium salts, 2,4,6-triarylsubstituted pyrylium salts drew much attention because three benzene rings as substituents in the two α- and the γ-positions provide enhanced stability by resonance, and they still exhibit moderate reactivity towards nucleophiles at the same time.[2] Moreover, 2,4,6-triarylpyrylium salts exhibit good physical properties and reactivity when compared to other alkyl-substituted or unsubstituted pyrylium salts.[1,2]

Although there has been a variety of synthetic methods reported for preparation of 2,4,6-triarylpyrylium salts, they can be conveniently prepared by two synthetic pathways based on substituent patterns in the pyrylium ring. First, one mole of benzaldehyde is condensed with two moles of acetophenone in the presence of a catalyst to yield 2,4,6-triphenylpyrylium salts, which is the simplest 2,4,6-triarylpyrylium salt. This procedure is probably the best method to synthesize a variety of 2,4,6-triarylpyrylium salts with identical groups in α- and γ-positions of the pyrylium ring as shown in Table 1. In some cases, perchloric acid was used as a second reagent to exchange the anions to perchlorate from hydrogensulfate or chloride anions due to difficult isolation of the product as mentioned previously. In this method, the substituents in 2-

Table 2. Reported synthesis of asymmetrically substituted 2,4,6-triarylpyrylium salts from α,β-unsaturated ketones and benzaldehyde



Ar_1	Ar_2	Ar_3	X	Conditions	Yield (%)	Mp (°C)	Ref
Ph	Ph	Ph	$FeCl_4$	$FeCl_3/Ac_2O$	30	277	9
Ph	Ph	Ph	BF_4	BF_3/Ac_2O	65	255-257	18, 19
Ph	Ph	Ph	ClO_4	1. H_2SO_4 2. $HClO_4$	80	266-268	20
4-ClC_6H_4	Ph	Ph	$FeCl_4$	$FeCl_3/Ac_2O$	34	279	21
4-$MeOC_6H_4$	Ph	Ph	$FeCl_4$	$FeCl_3/Ac_2O$	50	231-232	22
4-$MeOC_6H_4$	Ph	Ph	ClO_4	$POCl_3$	NA	236	13
4-$O_2NC_6H_4$	Ph	Ph	$FeCl_4$	$FeCl_3/Ac_2O$	40	218	23
Ph	Ph	4-Tol	$FeCl_4$	$FeCl_3/Ac_2O$	40	224	22
Ph	Ph	4-ClC_6H_4	$FeCl_4$	$FeCl_3/Ac_2O$	38	295	22
4-ClC_6H_4	4-ClC_6H_4	Ph	$FeCl_4$	$FeCl_3/Ac_2O$	34	265	21

NA = Not Available.

and 6-positions of the pyrylium ring are always identical based on methyl aryl ketones used while 6-position substituent is determined by benzaldehyde used. This synthetic method has the limitation in structural modification because the substituents in 2-position must be identical to 6-position. In 1919, Dilthey introduced the synthesis of 2,4,6-triphenylpyrylium tetrachloroferrate from the reaction of 1,3-diphenylprop-2-en-1-one (α,β-unsaturated ketone) and acetophenone in the presence of iron (III) chloride/acetic anhydride.[11] By following this synthetic method, a variety of asymmetrically substituted 2,4,6-triarylpyrylium salts can be synthesized as shown in Table 2. Since two phenyl groups in 1,3-diphenylprop-2-en-1-one determine the substituents in 2- and 6-positions of the 2,4,6-triarylpyrylium salts, ease of structural modification can be

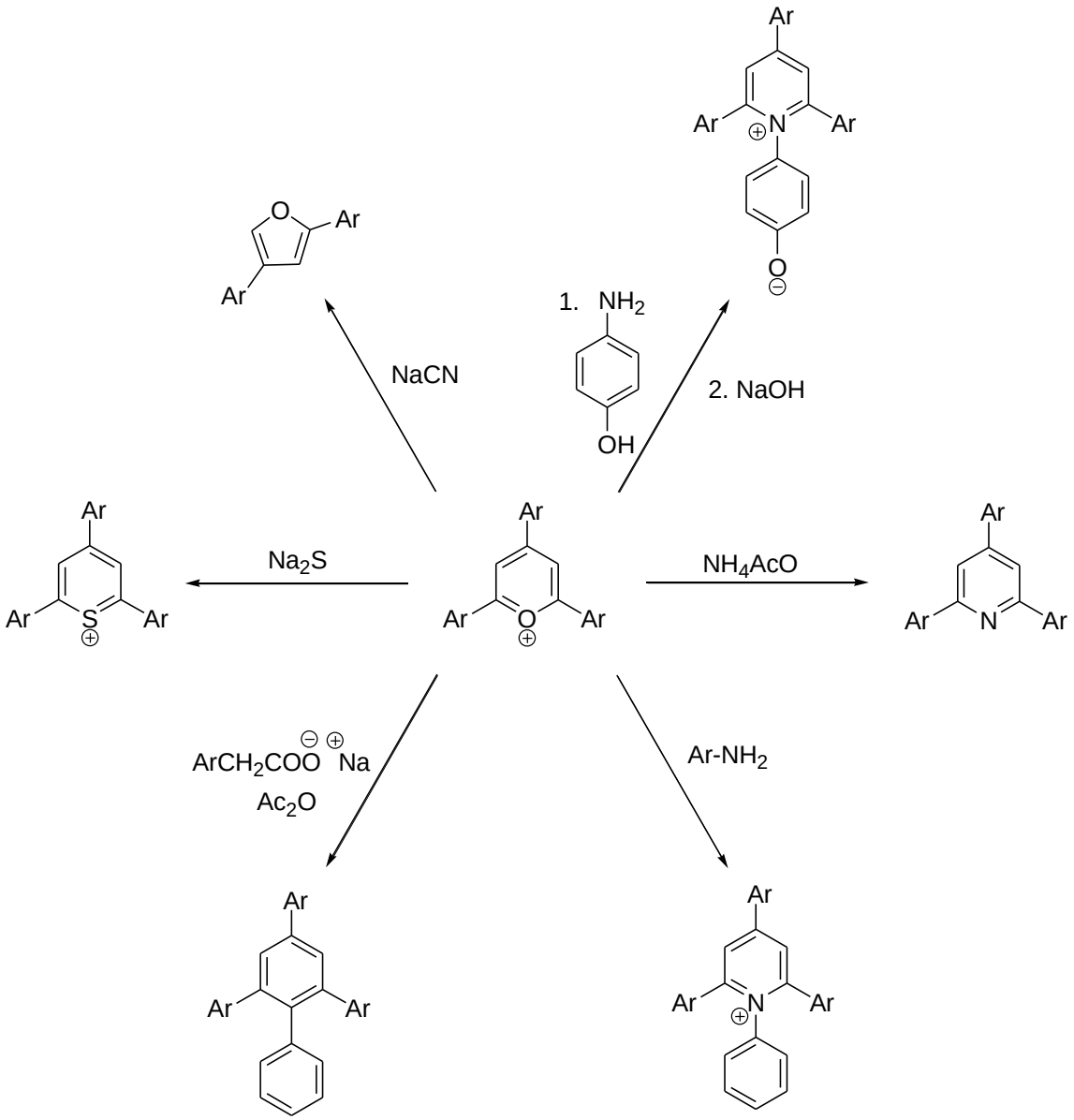


Figure 2. Chemical structures of representative organic molecules that can be synthesized from pyrylium salts.

accomplished by preparing asymmetrically substituted α,β-unsaturated ketones via acid- or base-catalyzed aldol condensation reaction.

Generally, pyrylium salts are an important class of heterocyclic compounds that are used in many synthetic routes, more than any heterocyclic compounds in organic chemistry. They are used as starting compounds in many variety of synthetic applications. These synthetic

applications arise because of their reactions with numerous nucleophiles. However, they do not undergo aromatic electrophilic substitution reactions because of the perturbation of aromaticity caused by the presence of a heteroatom. They also have significant interest in theoretical, pharmaceutical and materials chemistry because these salts are finding new applications in different fields of science and technology. As versatile synthetic precursors, they are of practical interest for complex heterocyclic moieties and for their intriguing physical properties. Figure 2 shows some of the representative examples of chemical transformation of pyrylium salts into different types of organic molecules, including substituted furan, pyridine, pyridinium salt, and betaine dyes, that have versatile applications.[26-30] In essence, they are the building blocks of synthesizing numerous complex chemical structures for functional materials.

Apart from the use of synthetic precursors in organic chemistry, pyrylium salts exhibit many outstanding photophysical properties that make them versatile in modern science and technology. The strong fluorescence of 2,4,6-triphenylpyrylium salts was first observed more than a century ago before pyrylium salts were known. In 1896, Kostanecki and Rossbach observed the strong green fluorescence of 1,3,5-triphenylpentane-1,5-dione in sulfuric acid that resulted 2,4,6-triphenylpyrylium salt, which was formed by cyclodehydrogenation in the presence of the acid.[24,25] In 1917, it was Dilthey who recognized that 2,4,6-triphenylpyrylium is responsible for the fluorescence property.[32] Figure 3 shows the chemical structures of various pyrylium salts that are employed for various applications. The electron accepting properties of these salts have resulted in diverse applications such as sensitizers for photo-induced electron transfer processes in many chemical transformations in photochemistry. The strong light emission properties of some salts, **I,** are responsible for their excellent lasing properties that would make possible for their use as lasers. Furthermore, they can exhibit a laser efficiency

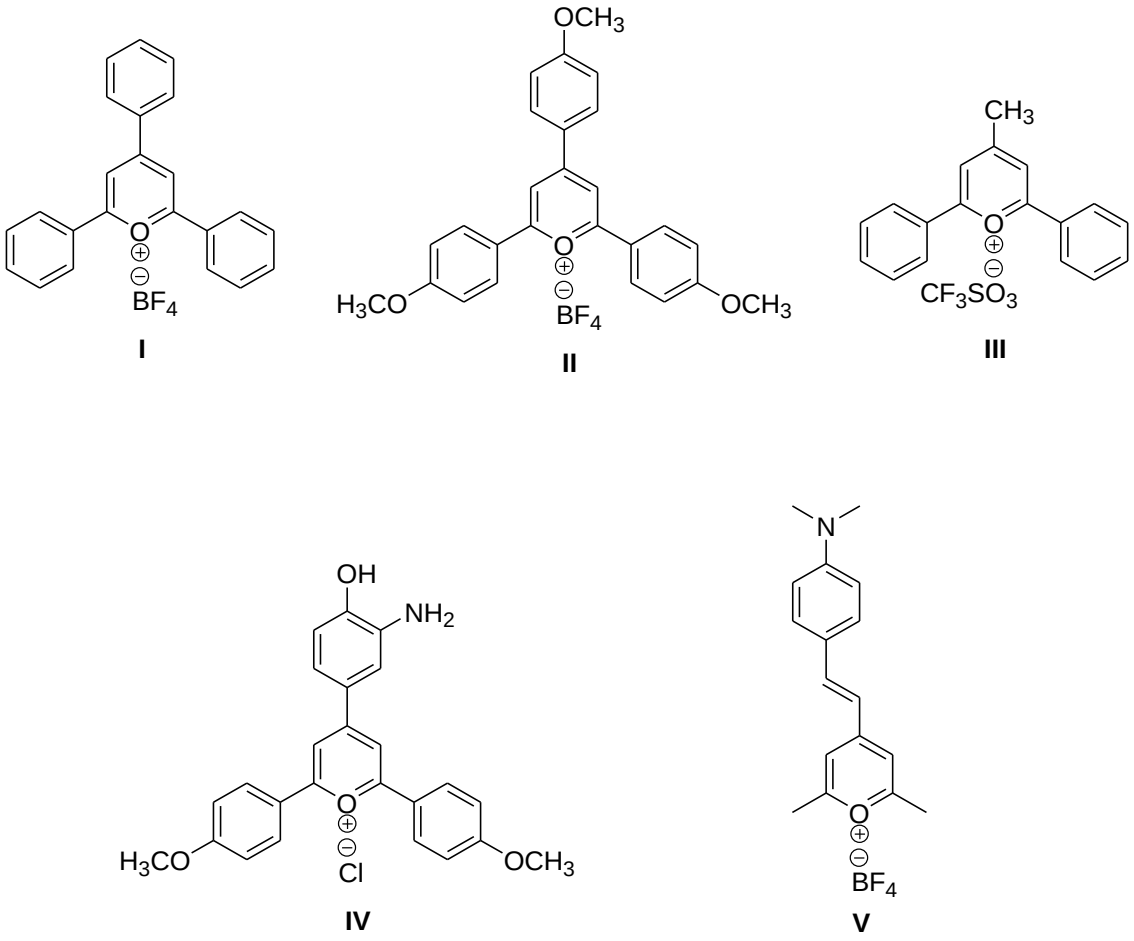


Figure 3. Chemical structures of pyrylium salts for various applications.

similar to Rhodamine 6G in dye lasers but expanding to an even wider range of tunable wavelengths.[33] Interestingly enough, some of the pyrylium salts, **II,** also exhibit two- and three-photon absoption properties. These multiphoton absorption materials have attracted a lot of interest over recent year because of their applications in various fields of physics, chemistry and biology. Three dimensional optical data storage, photodynamic therapy, upconverting lasers, optical power limiting micro- and nano-fabrications are some of the known applications of multiphoton technology.[34] Recently, the potential absorption, fluorescence and electron acceptor properties of these salts have been explored to design sensors or biosensors for anions; **III** for cyanide ion, **IV** for amines, amino acids, nitric oxide, and **V** for proteins.[35-37]

1.2. Objectives

The principal objective of this thesis is to synthesize 2,4,6-triphenylpyrylium salt and its various phenyl substituted salts with tosylate as counterions by using *p*-toluenesulfonic acid monohydrate (also known as tosic acid). In general, perchloric and tetrafluoroboric acid are used as common acid catalysts in order to prepare pyrylium salts of diverse chemical structures with ClO_4^- or BF_4^- as counterions. However, it is well known that perchloric acid poses explosion danger, and tetrafluoroboric acid poses difficult handling, problematic storage, and expensiveness. On the other hand, tosic acid is solid, relatively safe to handle, and an inexpensive reagent. In consequence, we explored tosic acid by several methods for the synthesis of pyrylium salts under different reaction conditions including solvent-free green synthetic approach. Although tosic acid has been used in many diverse organic transformations, it has not yet explored to date for the synthesis of pyrylium salts of diverse architectures with tosylate counterions. To mention a few of these transformations are esterification, protections and deprotections of aldehydes and ketones,[38] cyclotrimerization of both acetophenones and alkynes,[39] synthesis of polysubstituted quinolines[40, 41] from appropriate precursors, synthesis of oxazoles[42] from propargylic alcohols and amides, and rearrangement of dypnones[43] to 1,3,5-triarybenzenes. The chemical structures of pyrylium salts that were synthesized in this research are shown in Figure 4 and characterized by several spectroscopic techniques and elemental analysis. It was also of significant interest to examine the physical properties of these salts such as solubility in various organic solvents when compared with those with ClO_4^- or BF_4^- as counterions. The latter salts have limited solubility in organic solvents and have relatively ease of isolation because of their high crystallinity. The thermal properties and stabilities were determined by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA)

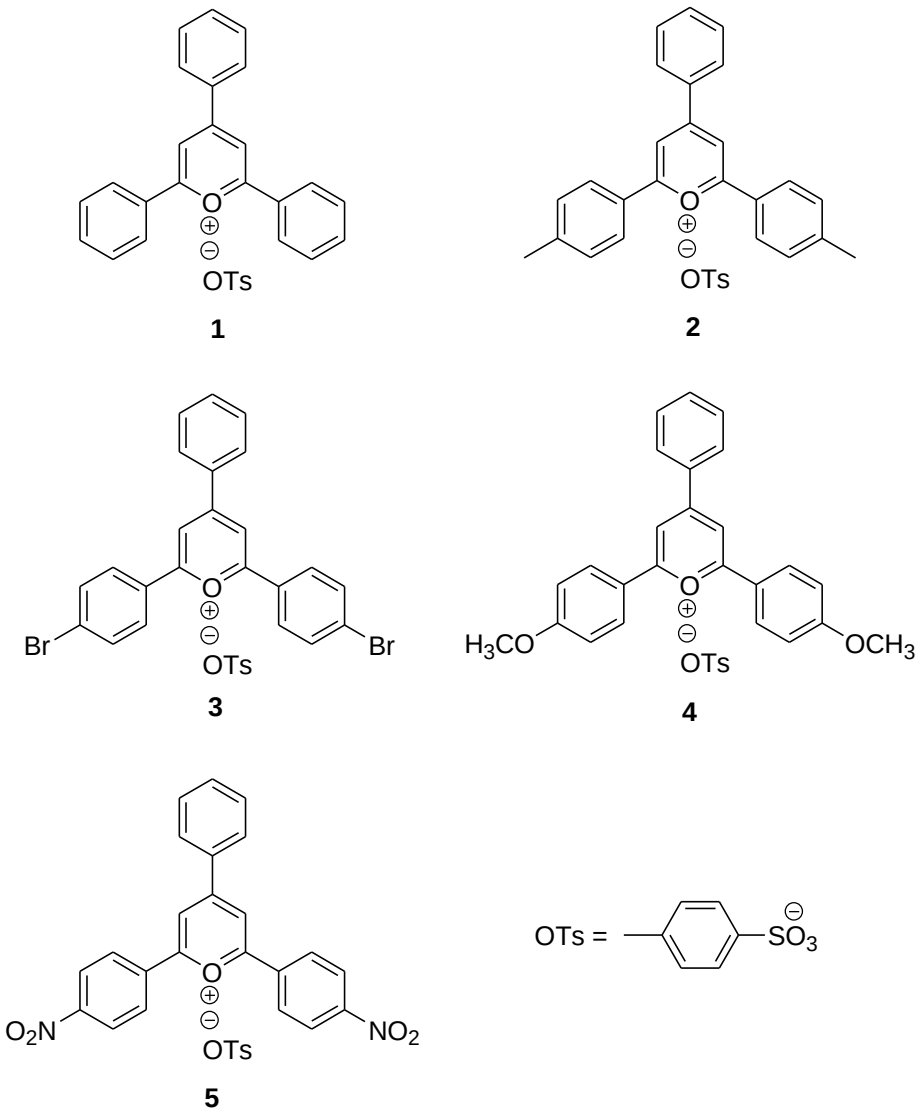


Figure 4. Structures of the pyrylium salts **1-5** of interest.

and contrasted with those salts with ClO_4^- or BF_4^- as counterions to examine the effect of tosylate counterions. Their optical properties both in solution and solid states were also studied by UV-Vis and luminescence spectrometers. Especially, there was significant interest of introducing electron donating substituents in para-positions of 2- and 6- phenyl rings of pyrylium salt show the substituents influenced their optical properties in solution as well as thermal properties. The salt **3** was targeted to see whether the presence of bromine atom could, in principle, increase the

triplet populations in photoexcited states of this salt by intersystem crossing due to heavy atom effect. We hoped, therefore, to see the phosphorescence of this salt rather than fluorescence.[44]

CHAPTER 2

MATERIALS AND METHODS

2.1. General Comments

All solvents and reagents including various acetophenones and benzaldehydes were purchased from commercial vendors (Sigma-Aldrich, Alfa-Aesar, Acro Organics, and TCI America) and used without any further purification.

^{1}H and ^{13}C NMR spectra were measured using a Varian NMR 400 spectrometer equipped with two RF channels at room temperature, and chemical shifts were reported in parts per million (ppm) relative to tetramethylsilane (TMS; δ 0.0) as the internal standard. The NMR sample solutions were prepared by dissolving 10 mg of ionic compounds in 1 mL of CD_3CN, $CDCl_3$, or DMSO-d_6. FTIR spectra were recorded with a Shimadzu spectrometer (IRAffinity-1), and samples were prepared as KBr pellets. The phase transition temperatures of ionic compounds were studied by using TA differential scanning calorimetry (DSC) Q200 series under nitrogen atmosphere at heating and cooling rates of 10 ℃/min. The temperature axis of the DSC thermograms was calibrated with reference standards of high purity indium and tin. The thermal properties of each compound was analyzed through thermal gravimetric analysis (TGA) using TA TGA Q50 under nitrogen atmosphere at a rate of 10 ℃/min in the temperature range between 30 and 800 ℃. The UV-Vis absorption spectra of ionic compounds were recorded using Varian Cary 50 Bio UV-Visible spectrophotometer in quartz cuvettes at room temperature. Photoluminescent properties in solution state were recorded by using a Perkin-Elmer LS 55

luminescence spectrometer with a xenon lamp as a light source. Quantum yields were calculated according to the following eq. (1):

$$\Phi_X = \Phi_{ST}\left(\frac{\text{Grad}_X}{\text{Grad}_{ST}}\right)\left(\frac{\eta^2_X}{\eta^2_{ST}}\right) (1)$$

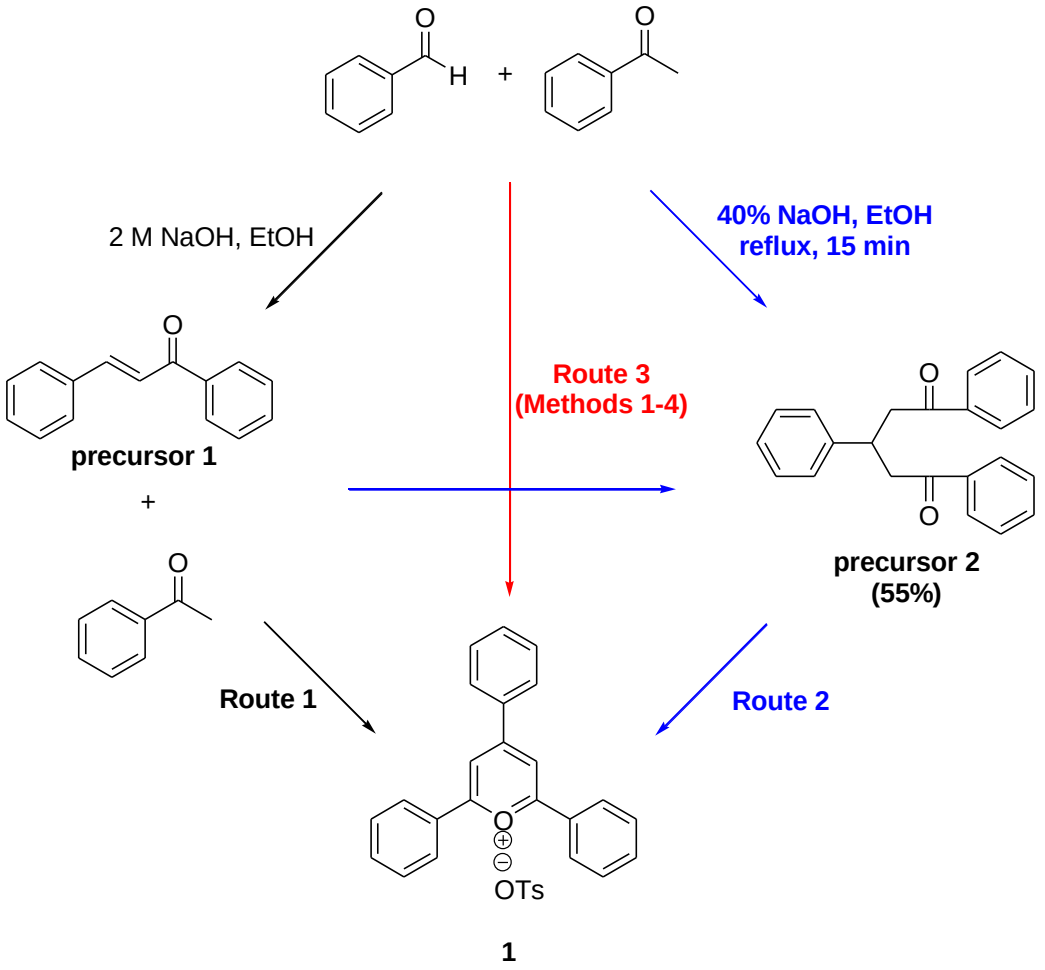
Where the subscripts ST and X denote the standard (9,10-diphenylanthracene) and unknown respectively, Φ is the fluorescence quantum yield, η is the refractive index of the solvent, and Grad is the gradient from the plot of integrated fluorescene intensity vs. absorbance of the minimum of five solutions prepared by serial dilution.[45]

2.2. Preparation of the Pyrylium Salt **1**

2.2.1. Synthetic Procedure for Route 1

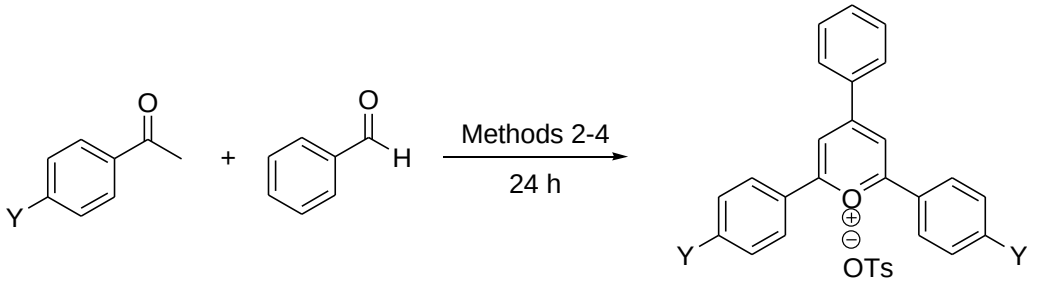
This procedure is an improved modification of that described by Dimroth for the synthesis of corresponding tetrafluoroborate salt.[46] The *p*-toluenesulfonic acid monohydrate (9.49 g, 49.9 mmol) was slowly added into a solution of *trans*-chalcone (10.4 g, 49.9 mmol), acetophenone (3.00 g, 25.0 mmol), and 20 mL of 1,2-dichloroethane while keeping the temperature at 50 ℃. The mixture was heated to reflux and stirring for 24 h. After the reaction was completed, the solution was concentrated by a rotary evaporator. The concentrated solution was poured into diethyl ether, and the crude product was collected by filtration and washed with diethyl ether. The crude product was purified by dissolving in the minimum of dichloromethane and precipitated in diethyl ether, and the final product was dried under vacuum oven to yield 3.96 g (8.24 mmol, 33%) of dark yellow solid. IR (KBr) ν (cm^{-1}) 3066, 2914, 1193, 1624, 1500, 1448, 1122, 1033, 767. ^{1}H NMR (400 MHz, DMSO-d_6) δ ppm 9.18 (s, 2H), 8.61 (d, *J* = 7.2 Hz, 2H), 7.89 (t, *J* = 7.6 Hz, 3H), 7.80-7.77 (m, 6H), 7.48 (d, *J* = 6.4 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ ppm 170.5, 165.5, 146.3, 137.9, 135.6,

Table3. Synthetic routes of 2,4,6-triphenylpyrylium tosylate



Route	Conditions		Temp	Time	Yield (%)
1	$TsOH \cdot H_2O$/1,2-dichloroethane		Reflux	24 h	33
2	Ph_3COH, $TsOH \cdot H_2O/Ac_2O$		100 ℃	2 h	88
3	Method 1	1. $POCl_3$ 2. $TsOH \cdot H_2O$/EtOH	1. 60 ℃ 2. rt	1. 8 h 2. 30 min	54
	Method 2	$TsOH \cdot H_2O$/toluene	Reflux	24 h	26
	Method 3	$TsOH \cdot H_2O$/1,2-dichloroethane	Reflux	24 h	28
	Method 4	$TsOH \cdot H_2O$	100 ℃	24 h	28

Table4. Synthesis of pyrylium salts **1-5**



1-5

Product	Y	Methods and Conditions		Temp (℃)	Yield (%)
1	H	Method 2	$TsOH \cdot H_2O$/toluene	reflux	26
		Method 3	$TsOH \cdot H_2O$/1,2-dichloroethane	reflux	28
		Method 4	$TsOH \cdot H_2O$	100 ℃	28
2	CH_3	Method 2	$TsOH \cdot H_2O$/toluene	reflux	16
		Method 3	$TsOH \cdot H_2O$/1,2-dichloroethane	reflux	19
		Method 4	$TsOH \cdot H_2O$	100 ℃	18
3	Br	Method 2	$TsOH \cdot H_2O$/toluene	reflux	25
		Method 3	$TsOH \cdot H_2O$/1,2-dichloroethane	reflux	23
		Method 4	$TsOH \cdot H_2O$	100 ℃	27
4	OCH_3	Method 2	$TsOH \cdot H_2O$/toluene	reflux	–[a]
		Method 3	$TsOH \cdot H_2O$/1,2-dichloroethane	reflux	11
		Method 4	$TsOH \cdot H_2O$	100 ℃	–[a]
5	NO_2	Method 2	$TsOH \cdot H_2O$/toluene	reflux	–[a]
		Method 3	$TsOH \cdot H_2O$/1,2-dichloroethane	reflux	–[a]
		Method 4	$TsOH \cdot H_2O$	100 ℃	–[a]

[a]Desired product was not obtained.

135.4, 132.9, 130.5, 130.3, 130.2, 129.5, 129.2, 128.4, 125.9, 115.6, 21.2. Elem. Anal. Calcd for $C_{30}H_{24}O_4S$ (480.57): C, 74.98; H, 5.03; S, 6.67. Found: C, 74.87; H, 5.16; S, 6.54.

2.2.2. Synthetic Procedure for Route 2

The precursor 2 (1,3,5-triphenyl-1,5-pentanedione) was prepared first by following an improved modification of that described by Hirsch.[47] The 40% aqueous sodium hydroxide (0.992 g, 24.8 mmol) was slowly added to a solution of acetophenone (2.98 g, 24.8 mmol) and benzaldehyde (1.00 g, 9.42 mmol) in ethanol. After the mixture was heated to reflux for 15 min, the solution was cooled to room temperature and 30 mL of water was added, whereupon a dark orange was settled to the bottom of the flask. The solution was kept and stirred in an ice bath until the oil turned into yellow solid. The crude product was collected and recrystallized from cold methanol to yield 1.70 g (5.18 mmol, 55%) of light yellow crystals. The *p*-toluenesulfonic acid monohydrate (1.45 g, 7.61 mmol) was slowly added to a mixture of 1,3,5-triphenyl-1,5-pentanedione (1.00 g, 3.05 mmol) and triphenylmethanol (1.98 g. 7.61 mmol) in 20 mL of acetic anhydride. After the mixture was kept at 100 ℃ for 2 h, it was cooled to room temperature and yellow precipitate was obtained by addition of 60 mL of water into the flask. The yellow solid was collected and washed with water to remove residual acid from the reaction. The identical purification procedure was followed as Route 1 to yield 1.30 g (2.71 mmol, 88%) of the pure product.[41]

2.2.3. Synthetic Procedure for Route 3-Method 1

This procedure is an improved modification of that described by Moghimi for the corresponding perchlorate salt.[48] The $POCl_3$(23.9 g, 103 mmol) was added slowly to a solution of

benzaldehyde (9.23 g, 87.0 mmol) and acetophenone (26.1 g, 218 mmol) in an ice bath. The solution was stirred and kept at 60 ℃ for 8 h. After cooling down, the solution was concentrated by a rotary vapor to remove excess $POCl_3$, and the viscous solution was dissolved by addition of ethanol. The *p*-toluenesulfonic acid monohydrate (20.7 g, 109 mmol) was slowly added to the solution at room temperature and kept on stirring for 30 min at room temperature. The ethanol was removed under vacuuo resulting black viscous solution, and yellow precipitate was obtained followed by addition of diethyl ether. The precipitate was collected and washed to remove excess *p*-toluenesulfonic acid monohydrate. The identical purification procedure was followed as Route 1 to yield 22.6 g (47.0 mmol, 54%) of the pure product.

2.2.4. Synthetic Procedure for Route 3-Method 2

This procedure is an improved modification of that described by Kotra for the corresponding tetrafluoroborate salt.[49] A mixture of benzaldehyde (0.883 g, 8.33 mmol), acetophenone (2.00 g, 16.7 mmol), and *p*-toluenesulfonic acid monohydrate (3.17 g, 16.7 mmol) in 5 mL toluene was heated to reflux for 24 h. The reaction flask was cooled to room temperature and the black viscous solution was poured into diethyl ether. The yellow precipitate was collected and washed with water to remove excess *p*-toluenesulfonic acid monohydrate. The identical purification procedure was followed as Route 1 to yield 1.04 g (2.17 mmol, 26%) of the pure product.

2.2.5. Synthetic Procedure for Route 3-Method 3

The identical synthetic procedure was followed as Route 3-Method 2 using 5 mL of 1,2-dichloroethane instead of toluene to yield 1.10 g (2.29 mmol, 28%) of the pure product.[46]

2.2.6. Synthetic Procedure for Route 3-Method 4

The identical synthetic procedure was followed as Route 3-Method 2 in solvent-free system at 100 ℃ to yield 1.13 g (2.35 mmol, 28%) of the pure product.[41]

2.3. Preparation of the PyryliumSalts **2-4**

2,6-bis(4-methylphenyl)-4-phenylpyrylium tosylate **2**: The identical synthetic procedures from Methods 2-4 of Route 3 were followed using 4′-methylacetophenone instead of acetophenone.[14] Yield = 16% (Method 2), 19% (Method 3), 18% (Method 4). IR (KBr) ν (cm^{-1}) 3061, 2914, 1620, 1500, 1193, 1120, 1033, 773. ^{1}H NMR (400 MHz, DMSO-d_6) δ ppm 9.05 (s, 2H), 8.57 (d, *J* = 7.2 Hz, 2H), 7.49 (d, *J* = 8.4 Hz, 4H), 7.87 (t, *J* = 7.6 Hz, 1H), 7.78 (t, *J* = 8.0 Hz, 2H), 7.60 (d, *J* = 8.4 Hz, 4H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ ppm 170.2, 164.8, 146.6, 146.3, 137.9, 135.3, 133.0, 130.9, 130.3, 130.1, 129.1, 128.4, 126.9, 125.9, 114.7, 21.9, 21.2. Elem. Anal. Calcd for $C_{32}H_{28}O_4S$ (508.63): C, 75.56; H, 5.55; S, 6.30. Found: C, 75.28; H, 5.62; S, 6.09.

2,6-bis(4-bromophenyl)-4-phenylpyrylium tosylate **3**: The identical synthetic procedures from Methods 2-4 of Route 3 were followed using 4′-bromoacetophenone instead of acetophenone.[14] Yield = 25% (Method 2), 23% (Method 3), 27% (Method 4). IR (KBr) ν (cm^{-1}) 3061, 2914, 1622, 1489, 1215, 1120, 1033, 767, 489. ^{1}H NMR (400 MHz, DMSO-d_6) δ ppm 9.18 (s, 2H), 8.61 (d, *J* = 7.6 Hz, 2H), 8.52 (d, *J* = 8.8 Hz, 4H), 7.98 (d, *J* = 8.4 Hz, 4H), 7.88 (t, *J* = 7.2 Hz, 1H), 7.77 (t, *J* = 8.0 Hz, 2H), 7.49 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ ppm 169.6, 165.6, 146.0, 138.0, 135.8, 133.3, 132.7, 131.0, 130.6, 130.2, 129.9, 128.6, 128.4, 125.9, 115.9, 21.2. Elem. Anal. Calcd for $C_{30}H_{22}Br_2O_4S$ (638.37): C, 56.44; H, 3.47; S, 5.02. Found: C, 56.42; H, 3.51; S, 4.88.

2,6-bis(4-methoxyphenyl)-4-phenylpyrylium tosylate **4**: The identical synthetic procedure from Methods 3 of Route 3 was followed using 4′-methoxyacetophenone instead of acetophenone.[13,14] After the reaction was complete, the solution was concentrated under vacuum. The minimum amount of acetonitrile was added to the flask to dissolve the dark viscous solution, and dark orange solid was precipitated out by addition of ice. The crude product was collected and recrystallized from chloroform to yield 537 mg (11%, 0.993 mmol). IR (KBr) ν (cm^{-1}) 3061, 2937, 1622, 1602, 1491, 1263, 1120, 1031, 773. ^{1}H NMR (400 MHz, DMSO-d_6) δ ppm 8.88 (s, 2H), 8.55 (m, 6H), 7.82 (t, *J* = 7.2 Hz, 1H), 7.76 (t, *J* = 7.2 Hz, 2H), 7.49 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 9.2 Hz, 4H), 7.11 (d, *J* = 8.0 Hz, 2H), 3.97 (s, 6H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ ppm 169.3, 165.2, 163.6, 146.2, 137.9, 134.9, 133.1, 131.4, 130.1, 130.0, 128.4, 125.9, 121.8, 115.8, 113.1, 56.5, 21.2. Elem. Anal. Calcd for $C_{32}H_{28}O_6S$ (540.63): C, 71.09; H, 5.22; S, 5.93. Found: C, 70.52; H, 5.25; S, 5.79.

CHAPTER 3

RESULT AND DISCUSSION

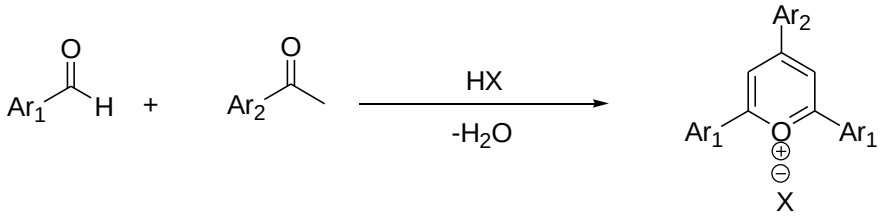
3.1. Synthesis of Organic Salts **1-5** and their Characterization

The pyrylium salt **1** was synthesized by three different routes in the presence of tosic acid as shown in Table 3. In the first route, 1,3-diphenylprop-2-en-1-one (*trans*-chalcone, precursor 1) can be easily prepared by an aldol-condensation reaction between acetophenone and benzaldehyde in the presence of a base catalyst such as sodium hydroxide. The precursor 1 was used to react with 1 mole of acetophenone via dehydrocyclization leading to the pyrylium salt **1**. In the second route, 1,3,5-triphenyl-1,5-pentanedione (precursor 2) was prepared from a base-catalyzed reaction between 1 mole of benzaldehyde and 2 moles of acetophenone, or from a Michael addition reaction of acetophenone to the precursor 1. The precursor 2 undergoes dehydrocyclization reaction, and triphenylmethyl cation generated from triphenylmethanol with tosic acid acts as a hydride ion acceptor to close the ring that leads to form the pyrylium salt **1**. Both the routes 1 and 2 can be widely used for syntheses of asymmetrically substituted 2,4,6-triarylpyrylium salts through preparation of precursors with desired groups of substituents. In the third route, pyrylium salt **1** was directly synthesized from 1 mole of benzaldehyde with 2 moles of acetophenone in four different methods. This route is one step process that involves formations of both the precursors 1 and 2 during the reaction. Identical substituents in 2- and 6-positions of pyrylium salts can be obtained based on the substituted acetophenones used. Table 3 shows four methods under different reaction conditions for the synthesis of **1**. These protocols were adopted and modified from the commonly used syntheses of symmetrically substituted

pyrylium salts via condensation and dehydrocyclization reactions from conventional acid catalysts such as perchloric acid and tetrafluoroboric acid. Method 1 used $POCl_3$ as a catalyst and generated in situ 2,4,6-triphenylpyrylium salt with chloride as a counterion, then it underwent a counterion exchange by the addition of tosic acid. Although this method resulted the descent yield (54%), removal of excess $POCl_3$ could be problematic during the workup because of its corrosiveness and the formation of hydrochloric acid by reacting with moisture in the air. Historically, benzene was first reported as a solvent for pyrylium salt synthesis using perchloric acid as a catalyst.[3] However, it was soon replaced by toluene due to its carcinogenicity. Therefore, in method 2, we adopted the identical reaction condition that used for a synthesis of pyrylium salt with perchlorate as a counterion. Perchloric acid was replaced by tosic acid with toluene as a solvent to obtain the pyrylium salt **1**. In method 3, we chose 1,2-dichloroethane as a solvent under the identical reaction condition as in method 2. This solvent was often used in synthesis in the route 1.[46] The pyrylium salt **1** has a good solubility in this solvent that provided the homogenous solution during the reaction and ease of clean workup process for the isolation of the product. In method 4, instead of using organic solvent, the synthesis of the pyrylium salt **1** was performed in the melt, which is solvent-free green synthetic approach. Lately, green chemistry has drawn much attention for reducing or eliminating the generation of hazardous substances or chemicals leading to environmental benefits and economic consideration. Tosic acid has been reported as a facile catalyst for solvent-free condensation reactions due to its low toxicity, operational simplicity, and inexpensiveness.[41] Method 4 was utilized for these beneficial aspects of tosic acid, and the % yield was comparable with other methods.

In all synthetic routes, the pyrylium salt **1** was easily isolated by addition of diethyl ether after completion of reactions. Since it is insoluble in diethyl ether due to its ionic character, other

Table 5. Reported synthesis of 2,4,6-triarylpyrylium salts from aryl methyl ketones and benzaldehydes



Ar_1	Ar_2	X	Conditions[a]	Temp (°C)	Time (h)	Yield (%)	Ref
Ph	Ph	ClO_4	$HClO_4$/toluene	110	NA	49	12
Ph	Ph	ClO_4	H_2SO_4	100	1	NA	13
Ph	Ph	BF_4	$BF_3 \cdot OEt_2$	100	2	40	14
Ph	Ph	$FeCl_4$	$FeCl_3$/AcOH	NA	NA	49	9
4-Tol	Ph	BF_4	BF_3/AcOH	NA	NA	50	15
4-Tol	Ph	BF_4	$BF_3 \cdot OEt_2$	100	2	40	14
4-Tol	Ph	$FeCl_4$	$FeCl_3/Ac_2O$	100	0.2	25	16
4-BrC_6H_4	Ph	BF_4	$BF_3 \cdot OEt_2$	100	2	38	14
4-$MeOC_6H_4$	Ph	ClO_4	H_2SO_4	100	1	NA	13
4-$MeOC_6H_4$	Ph	ClO_4	$POCl_3$	50	2	NA	13
4-$MeOC_6H_4$	Ph	BF_4	BF_3/AcOH	NA	NA	31	14
4-$O_2NC_6H_4$	Ph	BF_4	BF_3/AcOH	NA	NA	70	15

[a]Reaction with H_2SO_4 or $POCl_3$ was followed by treatment with 70% $HClO_4$. NA = Not Available.

impurities or byproducts can be washed away because of their high solubility in diethyl ether. It was then further purified by dissolving in minimum volume of dichloromethane (CH_2Cl_2) and subsequent reprecipitation with the addition of diethyl ether. Overall, the pyrylium salt **1** with

tosylate as a counterion was prepared in comparable yields to previously reported pyrylium salts with other inorganic counterions such as BF_4^-, ClO_4^-, and PF_6^- as shown in Table 5. In contrast to the BF_4^-counterion, the presence of a bulky tosylate counterion in the pyrylium salt **1** increases its solubility significantly in common organic solvents such as alcohols, acetonitrile (CH_3CN), chloroform ($CHCl_3$), dichloromethane (CH_2Cl_2) as well as dimethyl sulfoxide (DMSO).

Among these methods of the synthetic route 3, methods 2, 3, and 4 were chosen for the synthesis of 2,4,6-triarylpyrylium salts **2**-**5** with substituents in *para*-positions of 2- and 6-phenyl rings as shown in Table 4 including the pyrylium salt **1**. Initially, four different functional groups (-CH_3, -Br, -OCH_3, and -NO_2) in *para*-position of acetophenones were selected based on their electron donating or withdrawing characteristics. By following the identical procedures of each method, they were prepared in respectable yields except the pyrylium salt **5**. It was presumed that a strong electron withdrawing effect of -NO_2 group on the aromatic ring affected its ring closing process in the reaction, which is consistent with the result in the cyclotrimerization of p-nitroacetophenone in presence of tosicacid.[39] Although they were prepared in the identical manner as the pyrylium salt **1**, their purification processes were quite different, since they had different solubility in common organic solvents due to the characteristics of each substituent. The pyrylium salt **2** was easily purified by dissolving in CH_2Cl_2 and reprecipitating with the addition of diethyl ether as the pyrylium salt **1**, but the pyrylium salts **3** and **4** were purified by recrystallization from N,N-dimethylformamide (DMF) and chloroform ($CHCl_3$), respectively. It was evident that their intrinsic properties were affected by two additional substituents in *para*-positions of 2- and 6- phenyl rings of the 2,4,6-triarylpyrylium salts.

The FTIR, ^{1}H, and ^{13}C NMR spectra of the pyrylium salts **1**-**4** along with their elemental analysis data were consistent with the chemical structures of desired salts. The FTIR spectra of

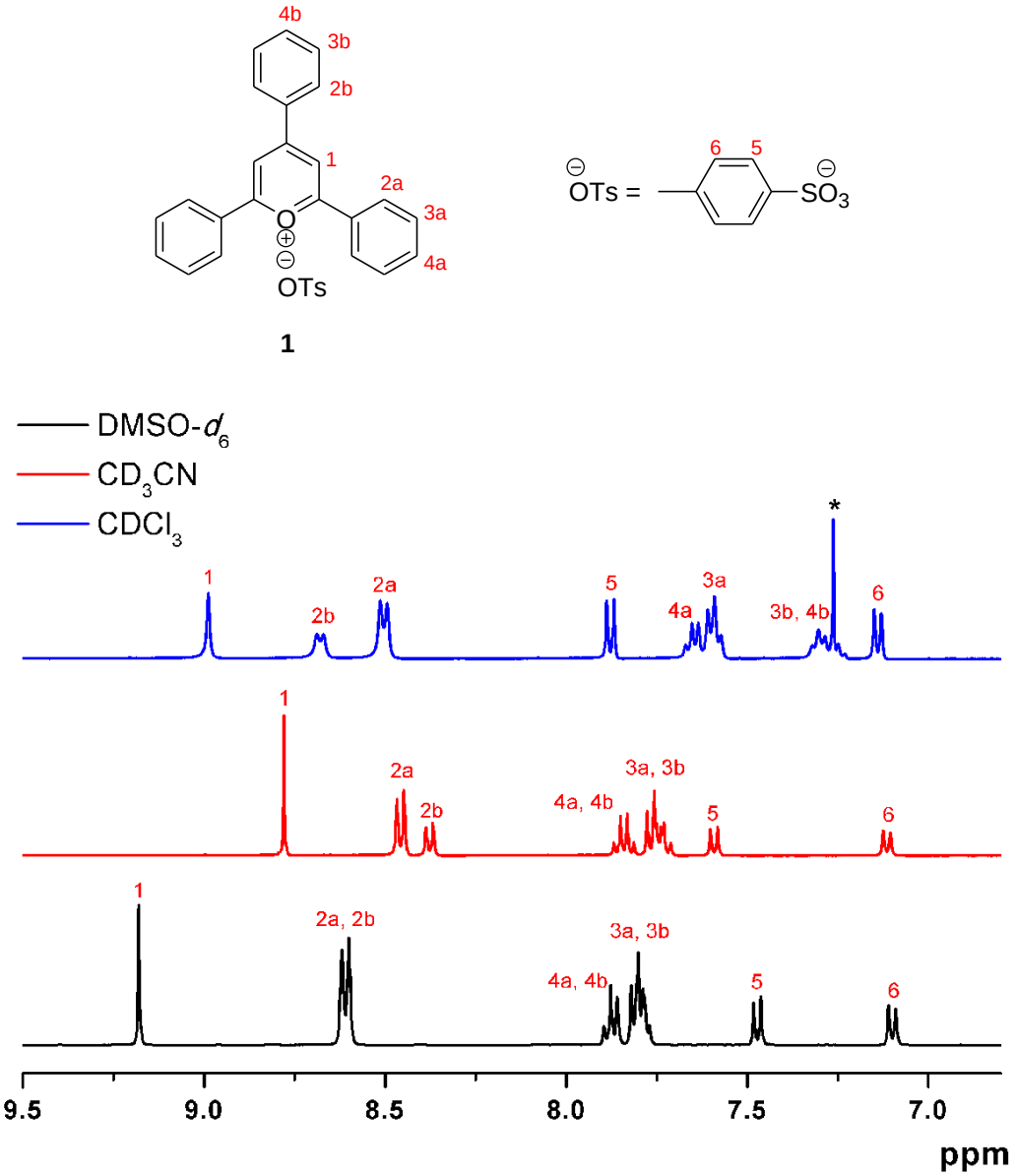


Figure 5. Expanded aromatic regions of ^{1}H NMR spectra of the pyrylium salt **1** in different deuterated solvents (An asterisk indicates $CDCl_3$).

the pyrylium salts **1**-**4** (Figure S1) showed the representative characteristic peaks: 1620–1624 ($C=O^{+}$ stretching), 1500–1516 (C=C aromatic stretching), 1120–1122 (S=O asymmetric stretching), 1031–1033 (S=O symmetric stretching), 767–773 cm^{-1} (S-O stretching).[30] Moreover, an additional C–Br stretching peak was observed at ν = 490 cm^{-1} in the pyrylium salt **3**. Especially, the enhanced solubility of the pyrylium salt **1** enabled ^{1}H NMR spectroscopic

analyses in different deuterated solvents (DMSO-d_6, CD_3CN, and $CDCl_3$). Figure 5 shows the ^1H NMR spectra of the pyrylium salt **1** in these solvents, and corresponding peaks were labeled. Overall, they showed similar signal patterns but their chemical shifts noticeably changed with the polarity of deuterated solvents. In DMSO-d_6, 2,4,6-triphenylpyrylium cation showed only four peaks at 9.18 (1), 8.48 (2a and 2b), 7.90 (4a and 4b), and 7.82 (3a and 3b) ppm. Interestingly, the protons 2a and 2b appeared together as one doublet although their electronic environments were different because 2a is located closer to the positively charged oxygen atom in the pyrylium ring. The identical phenomenon was observed between the protons 3a and 3b as well as 4a and 4b. In CD_3CN, which is relatively a less polar solvent than DMSO-d_6, chemical shifts of these protons were shifted to upfield with the same trend as in DMSO-d_6 except the protons 2a and 2b. These protons appeared separately as two doublets at 8.48 (2a) and 8.39 (2b) ppm that is in contrast with those in DMSO-d_6. In $CDCl_3$, which is the least polar solvent among the solvents examined, the protons 1, 2a, and 2b were shifted to downfield while the protons 3 and 4 were shifted to upfield. Especially, the proton 2b was significantly shifted to further down field at 8.69 ppm than the proton 2a at 8.51 ppm. It was interesting that the locations of the protons 2a and 2b in $CDCl_3$ were reversed when compared with those in CD_3CN. Additionally, the protons 3a and 3b appeared separately at 7.67 and 7.32 ppm, and the protons 4a and 4b also showed the identical behavior. As the polarity of solvents changed, not only the protons of the 2,4,6-triphenylpyrylium cation but also the protons of the tosylate anion showed changes in their chemical shifts. The proton 5 was shifted to more downfield at 7.48, 7.60, and 7.89 ppm, as solvent polarity changes from DMSO-d_6 to CD_3CN to $CDCl_3$, respectively, but the chemical shift of the proton 6 did not show any significant changes. Note here that change in chemical shifts of some carbon signals of this salt (not shown) was also observed in these deuterated

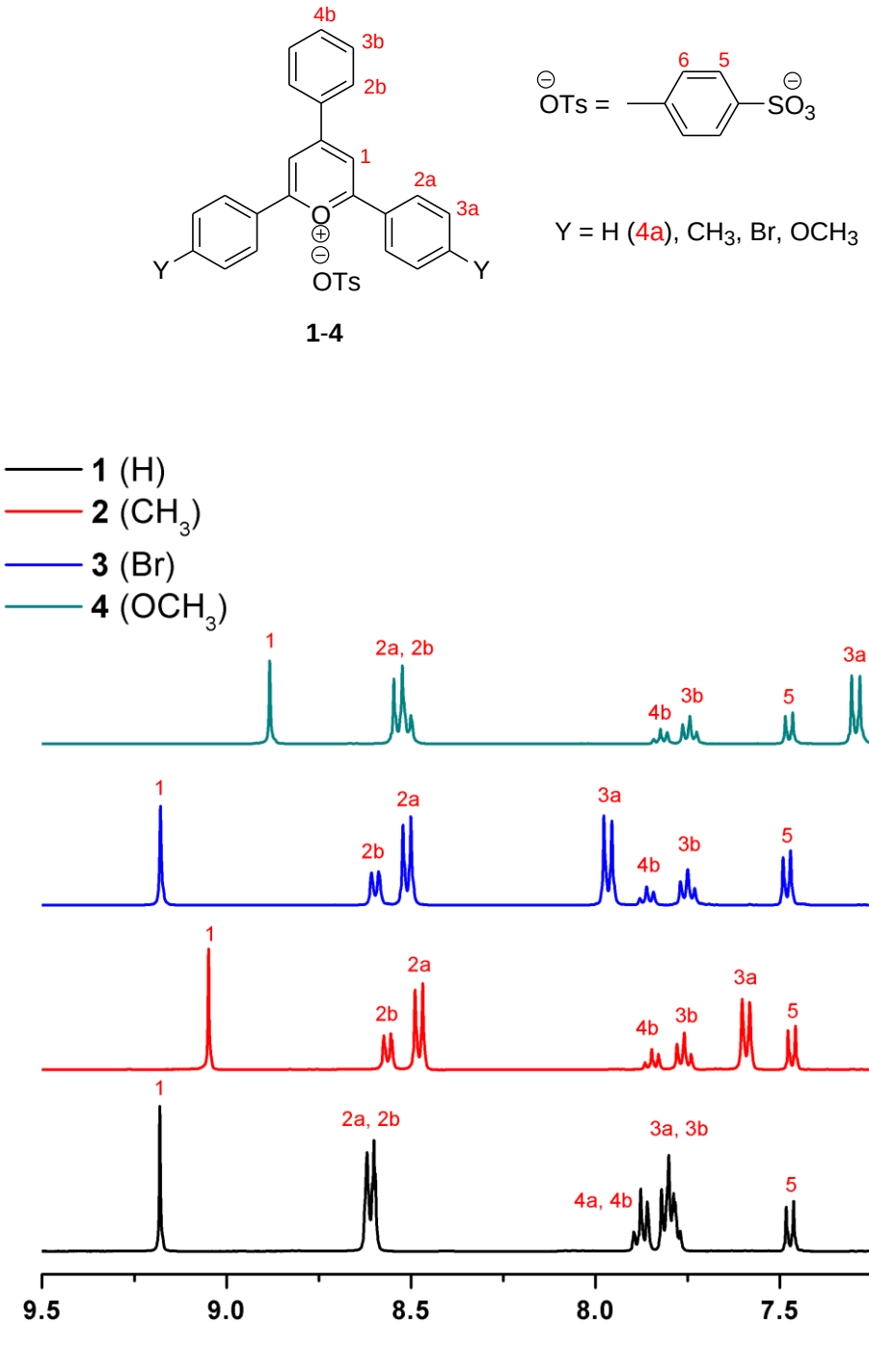
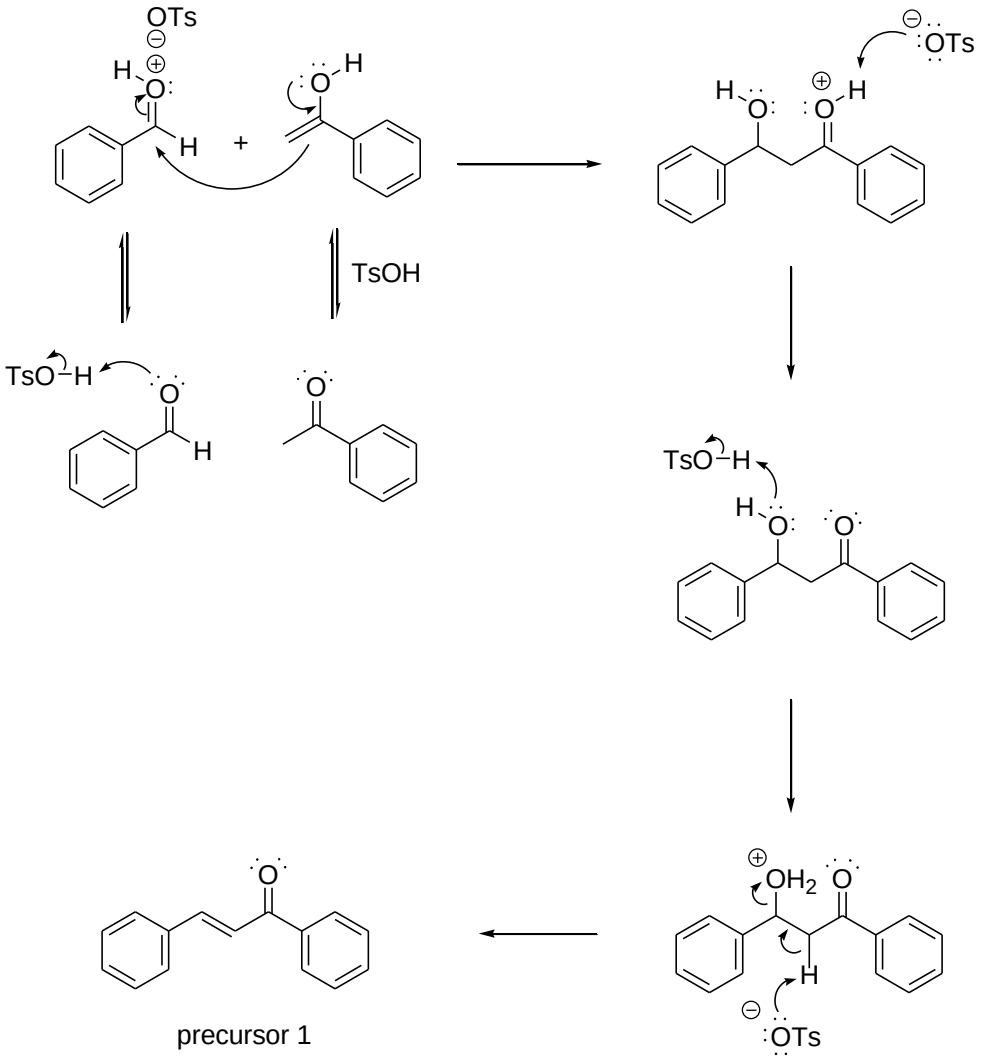


Figure 6. Expanded aromatic regions of ^{1}H NMR spectra of the pyrylium salts **1**-**4** in DMSO-d_6.

solvents. These interesting phenomenon of change in chemical shifts of an organic salt in different solvents suggest that the polarity of solvent has an effect on the extent of separation

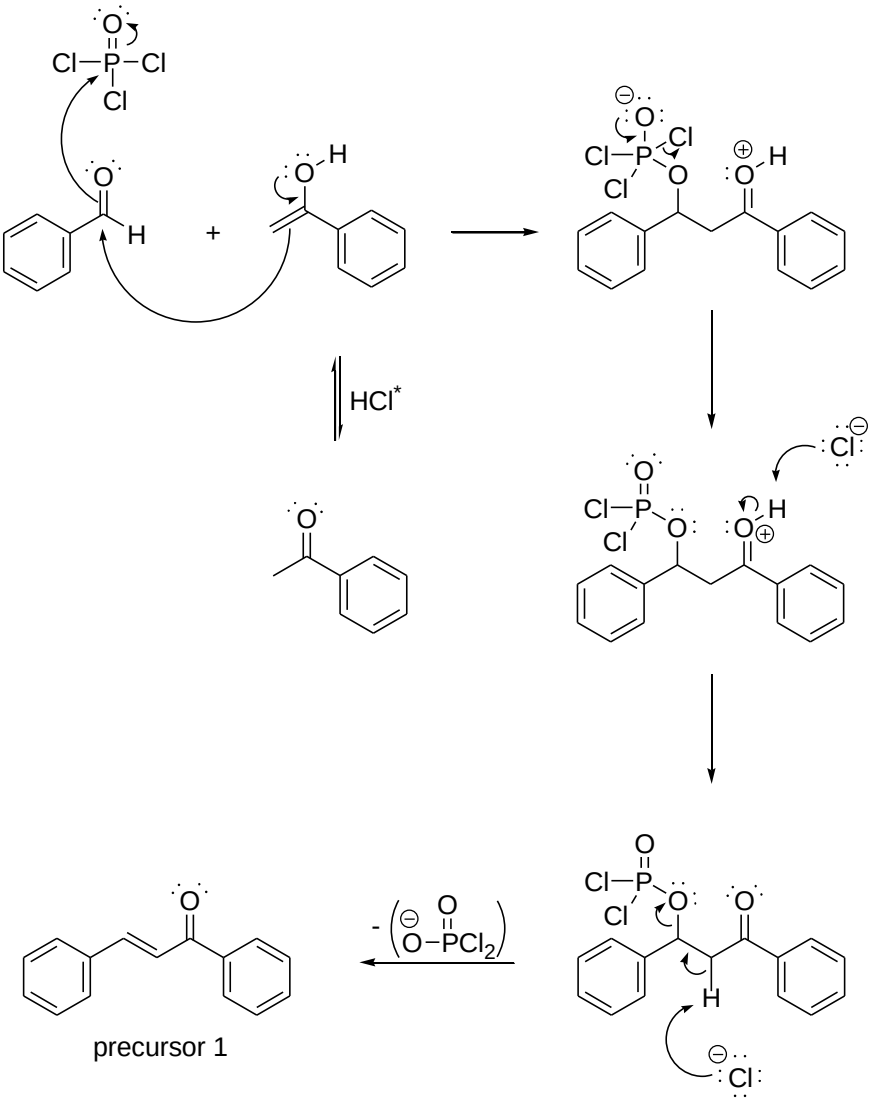
between 2,4,6-triphenylpryrylium cation and its counterion (tosylate) in solutions, which is consistent with the results of other ionic salts or poly(ionic salt)s . Ionic salts generally are more polar and their proton peaks are sensitive to the polarity of the solvents. Therefore, it is probable that these cationic protons could be affected by shielding/deshielding effect of the associated anions due to ion solvation and ion association in these solvents.[28b,50-54]

Since pyrylium salts **2-4** contain substituents on *para*-positions of 2- and 6-phenyl rings, their substituent effects on ^{1}H NMR chemical shifts were also studied in DMSO-d_6 solvent (Figure 6). The most significant chemical shift changes were detected in the proton 3a because of its closest location to the substituents. As discussed earlier, the chemical shift of the proton 3a of the pyrylium salt **1** was overlapped with the proton 3b at 7.82 ppm in the absence of any substituents. However, the presence of CH_3 and OCH_3 groups increased its electron density by shielding effect from their electron donating characteristics on the phenyl rings, so the proton 3a of the pyrylium salts **2** and **4** was shifted to upfield at 7.60 and 7.31 ppm, respectively. On the contrary, the proton 3a of the pyrylium salt **3** appeared more downfield at 7.98 ppm than the other pyrylium salts. Although bromine is known as an *ortho*/*para* director because of its ability to donate electrons to aromatic rings, it is also capable of withdrawing electrons. In the pyrylium salt **3**, the latter case was applied so that the proton 3a was shifted to downfield. The substituent effect was also observed on the other protons 1, 2a, and 2b of the pyrylium salts **2-4**. The proton 1 of the pyrylium salt **2** and **4** was shifted to upfield at 9.05 and 8.88 ppm, while there was no change in chemical shift for proton 1 in the pyrylium salt **3**. Additionally, the protons 2a and 2b appeared as two separate doublets at 8.60 and 8.52 ppm in the pyrylium salts **2** and **3**, respectively. These results from ^{1}H and ^{13}C NMR (Figures S2-S9) spectra were consistent with the chemical structures of the desired salts.



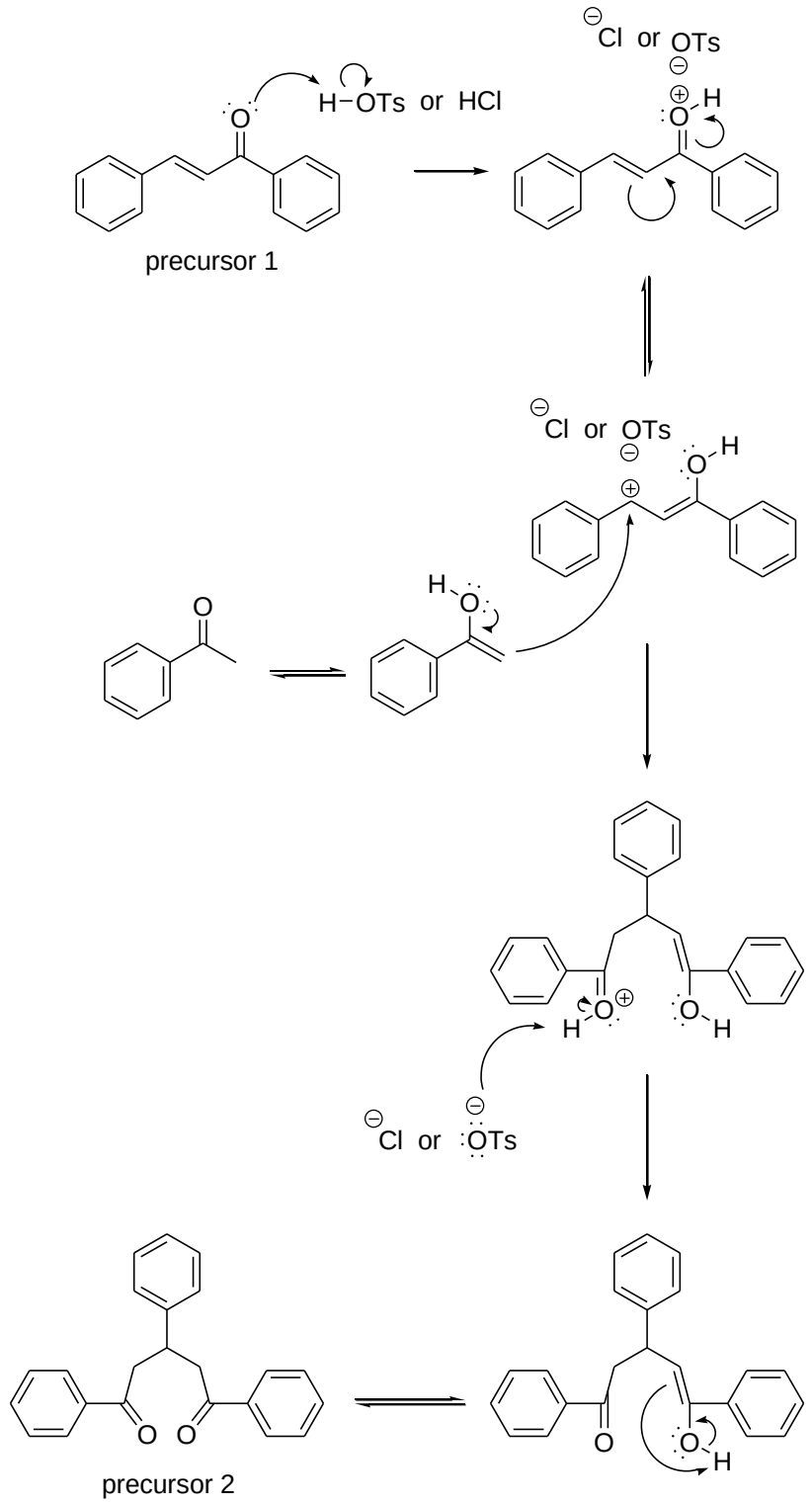
Scheme 1. Mechanism for the formation of 1,3-diphenylprop-2-en-1-one (precursor 1) using tosic acid as a catalyst.

The reaction mechanism for the synthesis of the pyrylium salt **1** using tosic acid or $POCl_3$ as a catalyst was proposed. As mentioned earlier, although the pyrylium salt **1** was synthesized in one step reaction (route 3), it involves the formation of the precursor 1 and 2 in situ during the reaction. Scheme 1 shows the formation of the precursor 1, which is the first intermediate product of the methods 2, 3, and 4 of the route 3 using tosic acid as a catalyst. An acid-catalyzed aldol condensation reaction takes place in order to form 1,3-diphenylprop-2-en-1-one (precursor 1). The most important step in this reaction is the formation of an enol, then it attacks

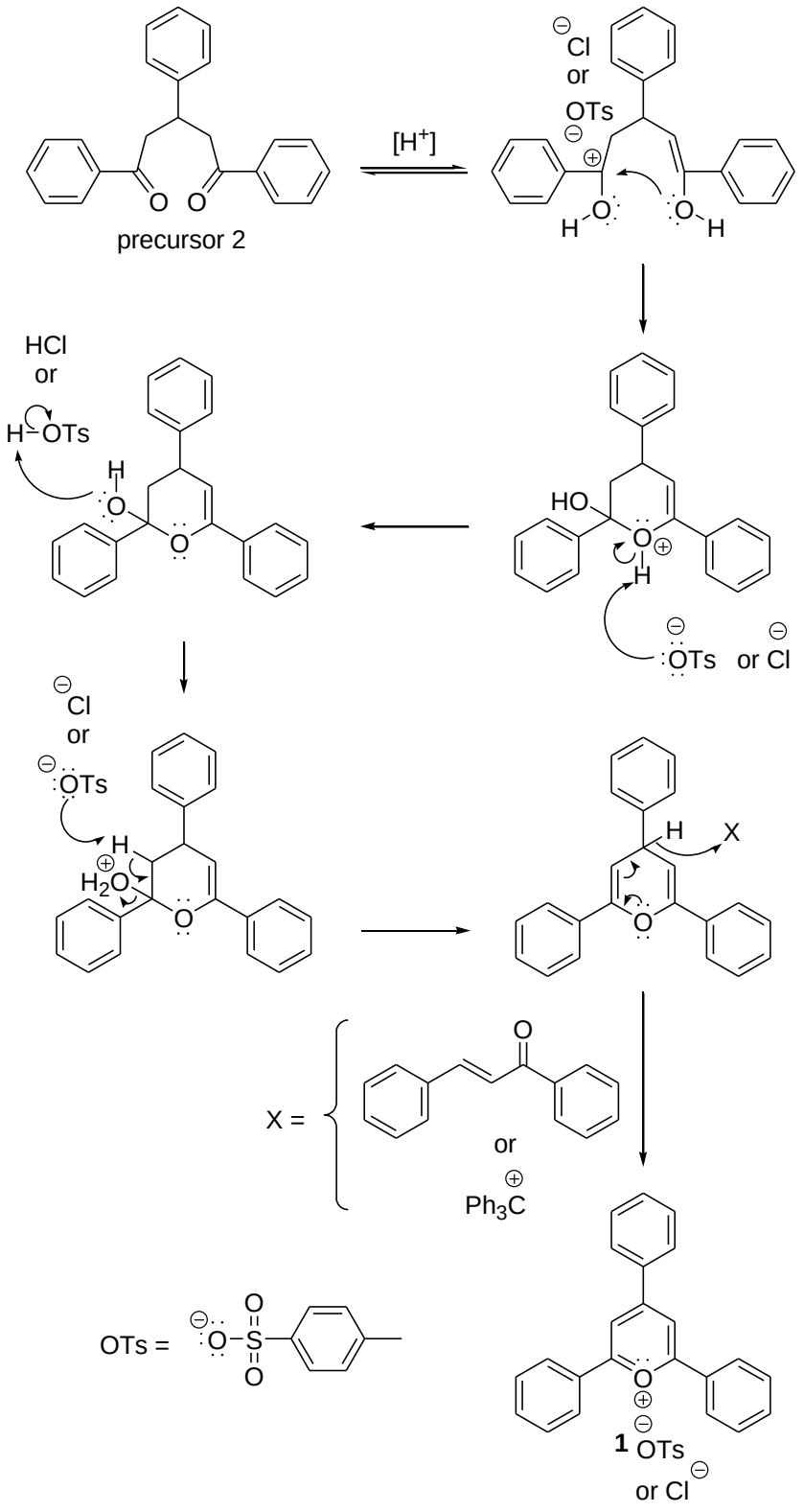


Scheme 2. Mechanism for the formation of 1,3-diphenylprop-2-en-1-one (precursor 1) using $POCl_3$ as a catalyst. *HCl is generated from a reaction of $POCl_3$ with the enol (acetophenone) or inadvertently in the presence of moisture in the reaction flask.

benzaldehyde to give an aldol product, which then dehydrates by an elimination reaction to generate an α,β-unsaturated carbonyl compound (precursor 1). Scheme 2 also shows the mechanism for the synthesis of the precursor 1 in the method 1 of the route 3 using $POCl_3$ as a catalyst. The reaction proceeds similarly as in Scheme 1, but hydrochloric acid is present and promotes the reaction instead of tosic acid. Hydrochloric acid is generated from a reaction of $POCl_3$ with an enol (acetophenone) or inadvertently in the presence of moisture in the reaction



Scheme 3. Mechanism for the formation of 1,3,5-triphenyl-1,5-pentanedione (precursor 2) from the precursor 1.



Scheme 4. Mehcanism for the dehydrocyclization reaction of the precursor 2 to form the pyrylium salt **1**.

flask. In Scheme 3, the precursor 1 undergoes a Michael addition reaction with another enol and forms 1,3,5-triphenyl-1,5-pentanedione (precursor 2). During this reaction, the enol would not simply add to the carbonyl carbon of the precursor 1 because the conjugation of a C=C bond with a C=O bond leads to a stabilizing interaction and modified reactivity, so that the π bond no longer reacts as independent functional group. According to the resonance structure of the precursor 1 in Scheme 3, the β carbon is positively charged and is attacked by the enol (nucleophile) leading to produce the precursor 2. The anions involved in this mechanism is determined as a tosylate or a chloride based on the catalyst used as shown previously in Scheme 1 and Scheme 2. Finally, an enol form of the precursor 2 undergoes dehydration and dehydrogenating cyclization to form the pyrylium salt **1** as shown in Scheme 4. If the pyrylium salt **1** is prepared by following the synthetic routes 1 and 3, the precursor 1 acts as a hydride acceptor (X) in order to complete aromatization of the pyrylium salt **1**. In the case of using $POCl_3$ (method 1) in the route 3, the pyrylium salt **1** is formed with a chloride as a counter anion first, and then tosic acid is used to exchange its counter anion to tosylate. On the other hand, in the synthetic route 2, a triphenylmethylcation is generated under acidic condition using tosic acid and acts as a hydride acceptor.

3.2. Thermal Properties of Organic Salts **1**-**4**

The thermal stability of the pyrylium salts **1**-**4** was studied by thermogravimetric analysis (TGA) in nitrogen and their plots are shown in Figures 7 and 8. In this study, the pyrylium salts with various substituents in the *para*-position of 2- and 6-phenyl rings had the decomposition temperatures (T_ds) in the range of 281 to 316 ℃. The pyrylium salt **1** had its T_d at 316 ℃, which was a higher decomposition temperature by 23 - 35℃ than those of the pyrylium salts with

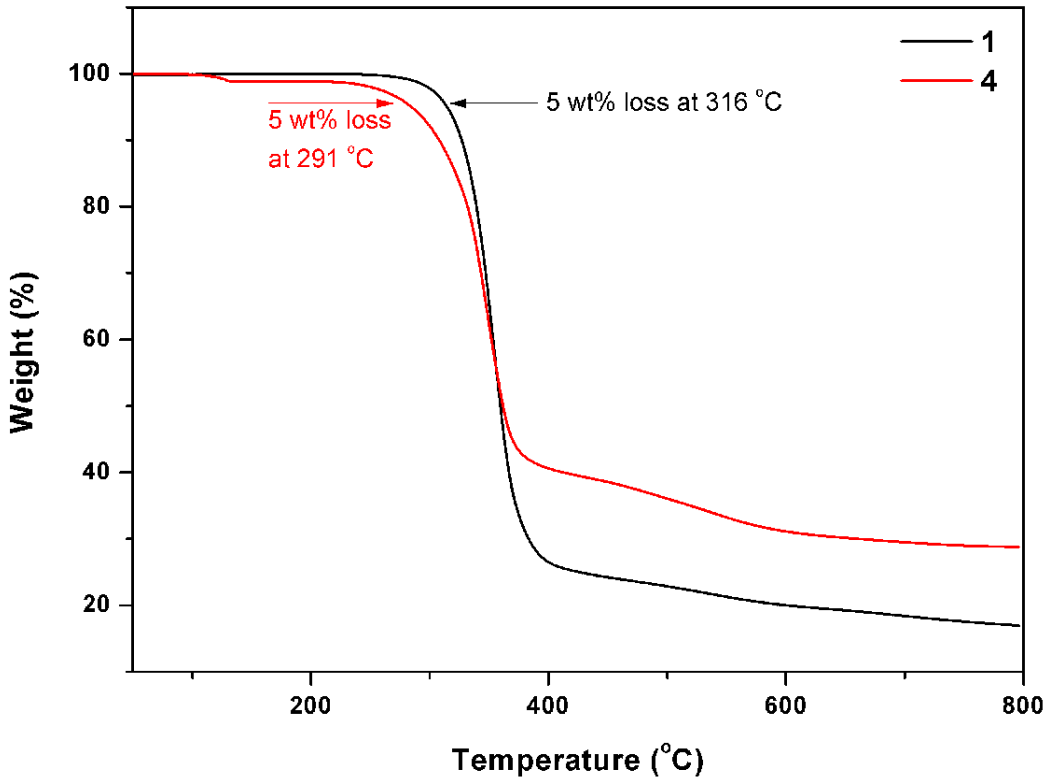


Figure 7. TGA thermograms of the pyrylium salts **1** and **4** in nitrogen at heating rate of 10 ℃/min.

substituents. The pyrylium salts **2** and **3** showed their T_ds at 281 ℃ and 293 ℃ (Figure 8), respectively, and their first derivative plots show that there are multiple decomposition steps unlike the pyrylium salt **1** and **4** (Figure 7). The pyrylium salt **4** had its T_d at 291 ℃ followed by the removal of entrapped water due to its hygroscopicity. The thermal transitions of the pyrylium salts **1**-**4** were studied by differential scanning calorimetry (DSC) measurements. Their thermal properties were also affected by the presence of substituents in para-positions of 2- and 6-phenyl rings. The pyrylium salt **1,** which has no substituent, showed a melting endotherm (T_m) at 222 ℃ with a heat of melting of 80.52 J/g in the first heating cycle and a recyrstallization exotherm (T_c) at 182 ℃ in the first cooling cycle. Correspondingly, there was a T_m at 215 ℃ with a heat of melting of 53.51 J/g in the second heating cycle, albeit at lower temperature than in the first

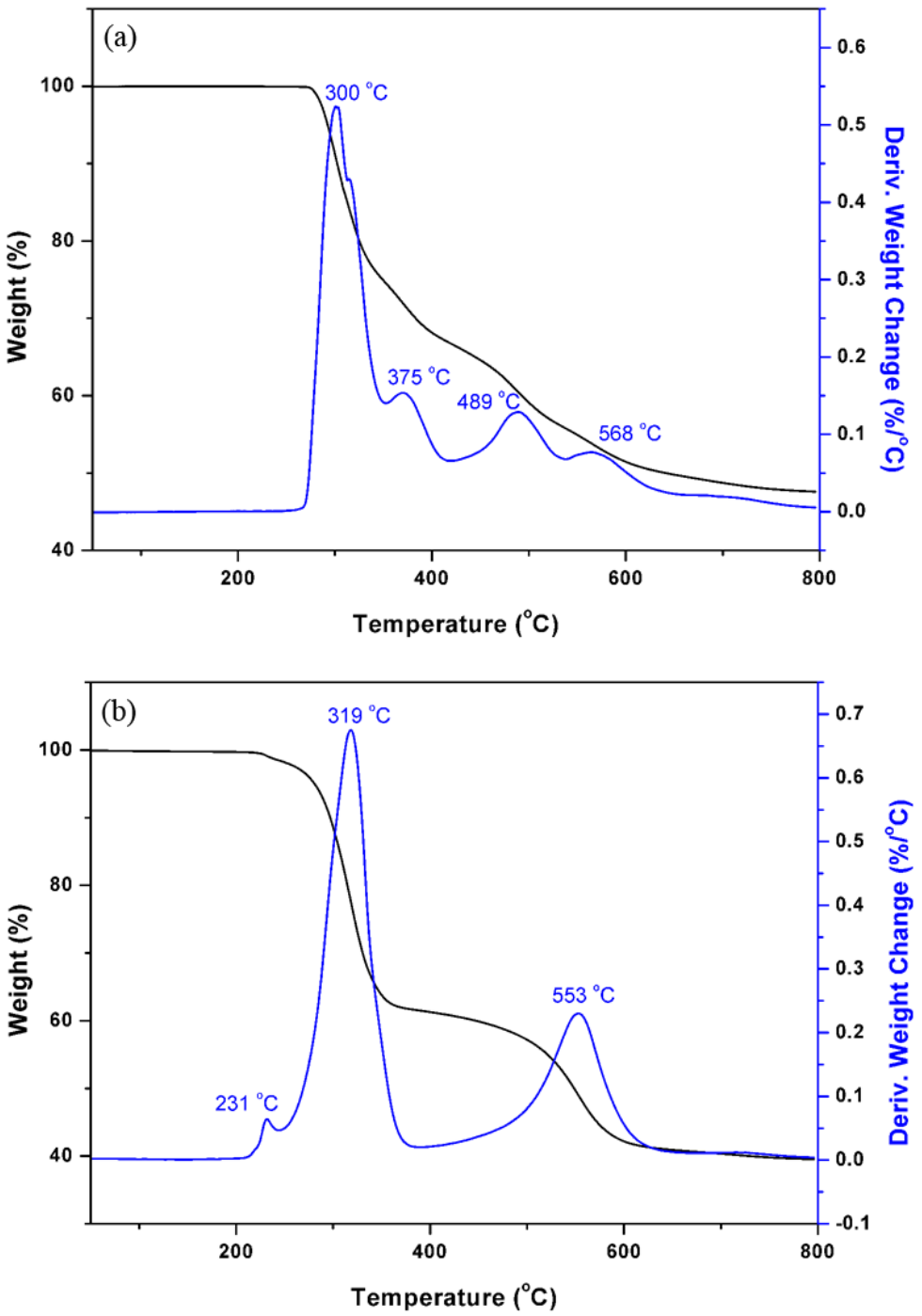


Figure 8. TGA thermograms of the pyrylium salts (a) **2** and (b) **3** with their first derivatives in nitrogen at heating rate of 10 ℃/min.

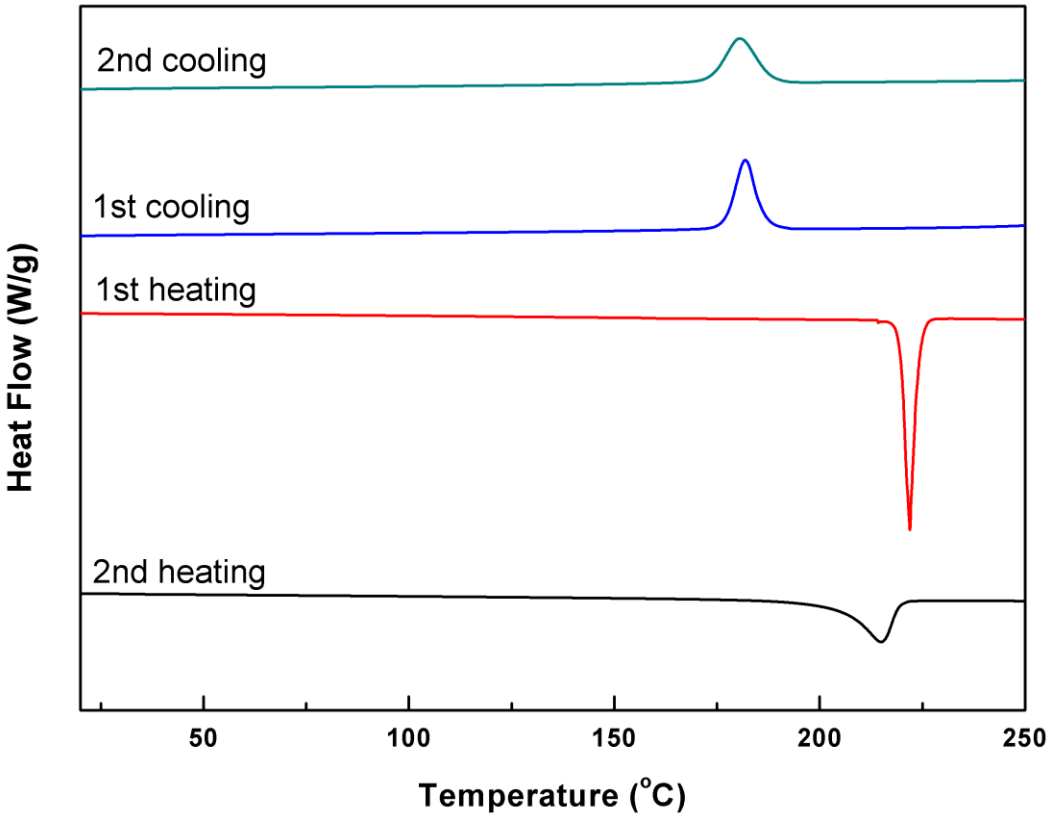


Figure 9. DSC thermograms of the pyrylium salt **1** obtained at heating and cooling rates of 10 ℃/min in nitrogen.

heating cycle. In the second cooling cycle, its T_c remained essentially identical to that in the first cooling cycle (Figure 9). These results suggested that this salt was less crystalline than that of solvent-induced crystal because of the bulky tosylate ion rendered difficulty in the crystallization from the melt. The pyrylium salts **2** and **3** showed their T_ms at 219 ℃ and 268 ℃, respectively. The presence of two methyl groups in the pyrylium salt **2** lowered the both melting point and decomposition temperature by 3 ℃ and 35 ℃, respectively. On the other hand, the pyrylium salt **3** that contains two bromine atoms showed the highest melting point among the synthesized pyrylium salts, but its decomposition temperature was still lower than the pyrylium salt **1**. In cases of both the pyrylium salts **2** and **3,** the second heating and cooling cycles could not be measured because their decomposition temperatures were close to the melting points. The

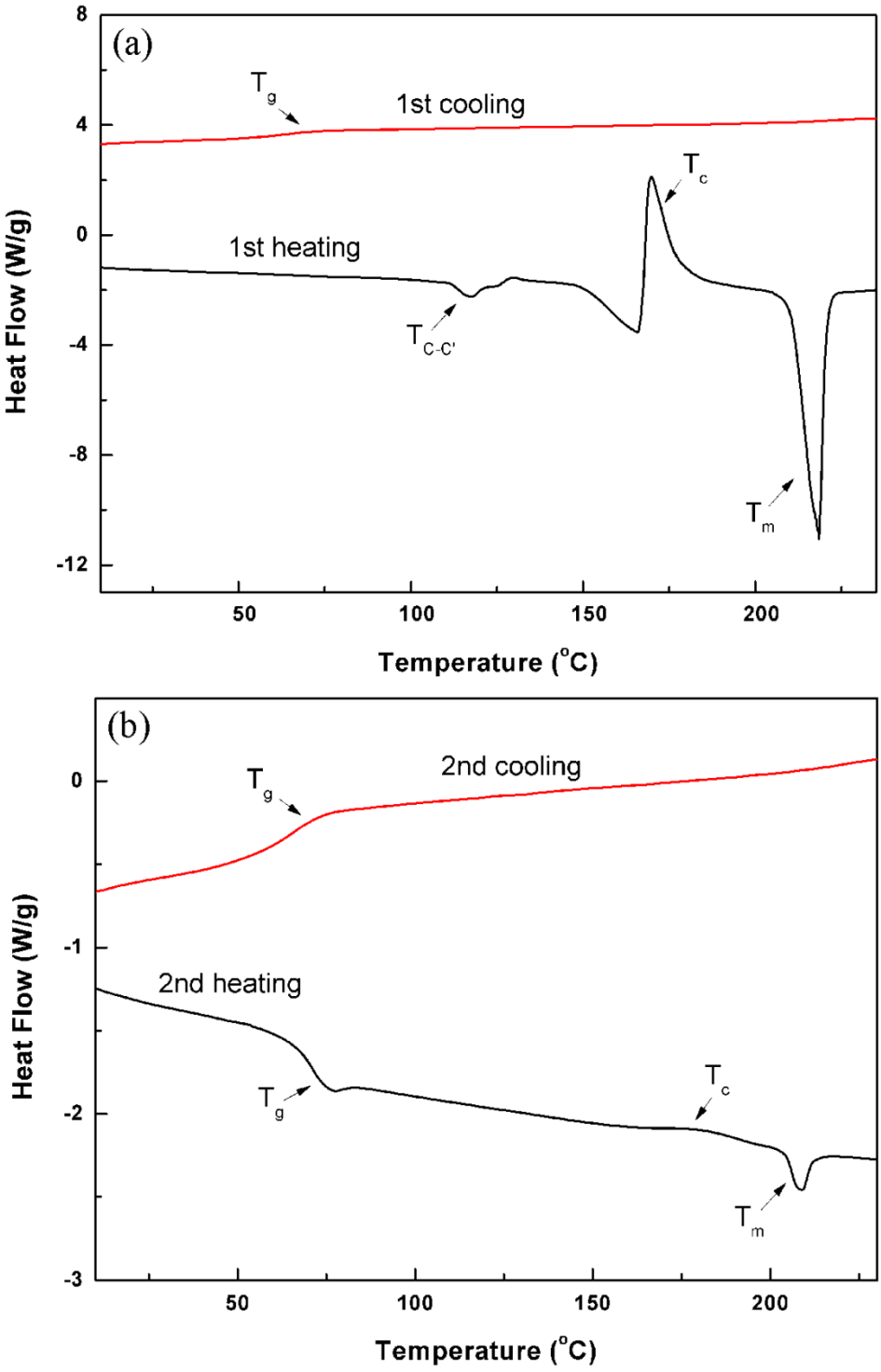


Figure 10. DSC thermograms of the pyrylium salt **4** obtained at heating and cooling rates of 10 ℃/min in nitrogen.

pyrylium salt **4** showed a low-temperature endotherm that corresponded to a crystal-crystal transition ($T_{C\text{-}C'}$), a cold crystallization exotherm at 170 ℃ followed by high-temperature endotherm at its T_m at 218 ℃ in the first heating cycle, which suggested the solvent-induced polymorphism properties of its crystalline phase. This phenomenon is quite common in many organic salts and liquid-crystalline organic salts.[55-59] After melting the solvent-induced crystals, a distinct glass transition (T_g) was observed at 71 ℃, but no cooling exotherm in the cooling cycle which suggested that it did not recrystallize under the experimental conditions used. In the second heating cycle, it showed a T_g, a barely noticeable cold crystallization exotherm prior to its T_m at 209 ℃ with the significantly reduced heat of melting (Figure 10). These results suggested **4** had the tendency to form an amorphous phase instead of crystalline phase. The melting transitions of all the ionic salts were lower than those of pyrylium salts containing perchlorate,[12] tetrafluoroborate,[14] and hexafluorophosphate as expected, since the bulky organic anion such as tosylate lowers the melting point of organic salts than that of the inorganic counterions.

3.3. Optical Properties of Organic Salts **1**-**4**

In general, highly rigid materials that consist of aromatic rings have limited solubility,[60,61] but all of the pyrylium salts herein except **3** had relatively good solubility in common organic solvents. They were dissolved into low polarity solvents such as chloroform, dichloromethane, and THF as well as high polarity solvents such as methanol, acetonitrile, and DMSO. Among these solvents, acetonitrile was chosen for the optical properties since the pyrylium salt **3** showed very limited solubility in the other organic solvents. The optical properties[62-65] of the pyrylium salts **1**-**4** including UV-Vis absorption, photoluminescence spectra and quantum yields in acetonitrile (CH_3CN) were compiled in Table 6. According to the previously reported studies of

Table 6. Optical properties of the pyrylium salts **1-4**

Entry	**1**	**2**	**3**	**4**
UV abs (nm)	275, 354, 404	287, 360, 429	287, 365, 420	319, 375, 470
Molar absorptivity ($M^{-1}cm^{-1}$)	ε_{275}= 19000 ε_{354} = 34000 ε_{404} = 26000	ε_{287}= 24000 ε_{360} = 36000 ε_{429} = 29000	ε_{287}= 21000 ε_{365} = 40000 ε_{420} = 32000	ε_{319}= 28000 ε_{375} = 37000 ε_{470} = 34000
PL λem CH_3CN (nm)	450	478	473	536
HOMO–LUMO gap (eV)[a]	2.89	2.66	2.78	2.46
Stokes shift (nm)[b]	46	49	53	66
fwhm CH_3CN (nm)	54	64	63	70
Φ_F (%) CH_3CN[c]	56	47	27	33

[a] Intersection of the absorption and emission spectra (Figures S18-21) corresponded to HOMO–LUMO gap (Highest occupied molecular orbital–Lowest unoccupied molecular orbital).
[b] Difference between emission maxima and the largest wavelength maxima of absorption maxima.
[c] Quantum yield was calculated against diphenyl anthracene as standard (Φ_F= 0.9).

2,4,6-triphenylpyrylium perchlorate, two absorption peaks at 417 and 369 nm were reported in CH_2Cl_2, and each absorption occurs due to two independent chromophores from two substructures, namely, the 2,6-diphenylpyrylium (longer wavelength) and the 4-phenylpyrylium (shorter wavelength) moieties, respectively.[33,66] The absorption spectrum of the pyrylium salt **1** in CH_3CN (Figure 11) is similar in appearance to that of the 2,4,6-triphenylpyrylium perchlorate in CH_2Cl_2, but its λ_{max} peak exhibited hypsochromic shifts caused by the increased solvent polarity. Similarly, **2-4** also showed hysochromic shifts in acetonitrile when compared with those in CH_2Cl_2.[66] In the pyrylium salt **2** when compared with **1** small bathochromic shifts of 12 and 6

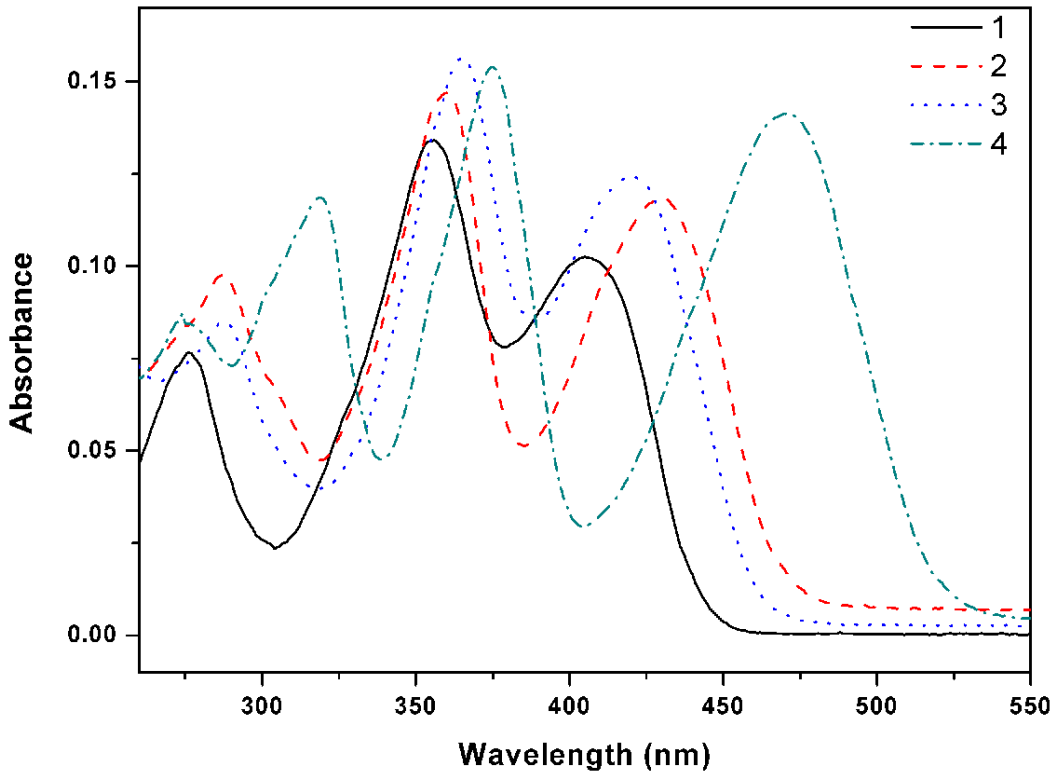


Figure 11. UV-vis spectra of the pyrylium salts **1-4** recorded in CH_3CN with the concentration of 4×10^{-6} M.

nm in the shorter wavelengths and large bathochromic shift of 25 nm in the longer wavelength. Similarly, **3** showed small bathochromic shifts of 12 and 11 nm in the shorter wavelengths and large bathochromic shift of 16 nm in the longer wavelength. The pyrylium salt **4** contains two methoxy groups (strong donor strength) bearing in 2- and 6-phenyl rings showed significant bathochromic shifts of 44 and 21 nm at the shorter wavelength and 66 nm at the longer wavelength since the 2,6-diphenylpyrylium substructure is responsible for the absorption of the longer wavelength. These results confirmed that substituent of strong electron donating effect caused significant changes in the longer wavelength absorption in the 2,4,6-triphenylpyrylium cation, because the primary chromophore is only available in the cation. These salts had relatively large absorption coefficients in the range of 19000-40000 $M^{-1}cm^{-1}$ (Table 6, Figures S10-S13), which are in good agreement with the results of corresponding pyrylium

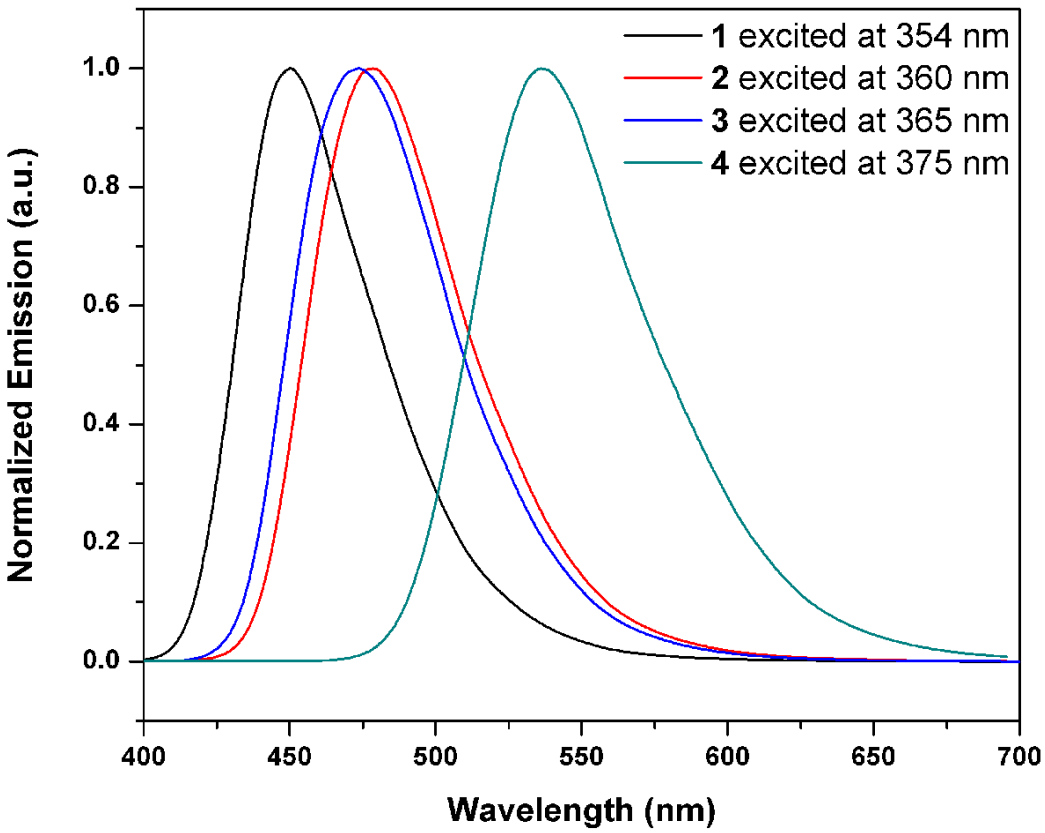


Figure 12. Emission spectra of the pyrylium salts **1**-**4** recorded in CH_3CN at various excitation wavelengths.

perchlorates.[66] Note here that the recoded excitation spectra of these salts (Figures S14-S21) faithfully reproduced their UV-vis absorption spectra that provided the compelling evidence for their photoluminescence properties in acetonitrile. The light emission spectra of the pyrylium salts **1**-**4** in CH_3CN are shown in Figure 12. The pyrylium salts **1**-**3** emitted blue light with λ_{em} values in the range of 450–478 nm when excited at various wavelengths, and these values indicate that the variation of the substituents in 2- and 6-phenyl rings had an effect on the light emission properties. However, the pyrylium salt **4** showed a significant bathochromic shift and emitted green light with λ_{max} at 536 nm when excited at 375 nm (Figure 13). The HOMO-LUMO gaps of these salts as calculated from the intersections of absorption spectra and emission spectra (Figures S18-S21) were found to be 2.89, 2.66, 2.78, and 2.46 eV, respectively. The

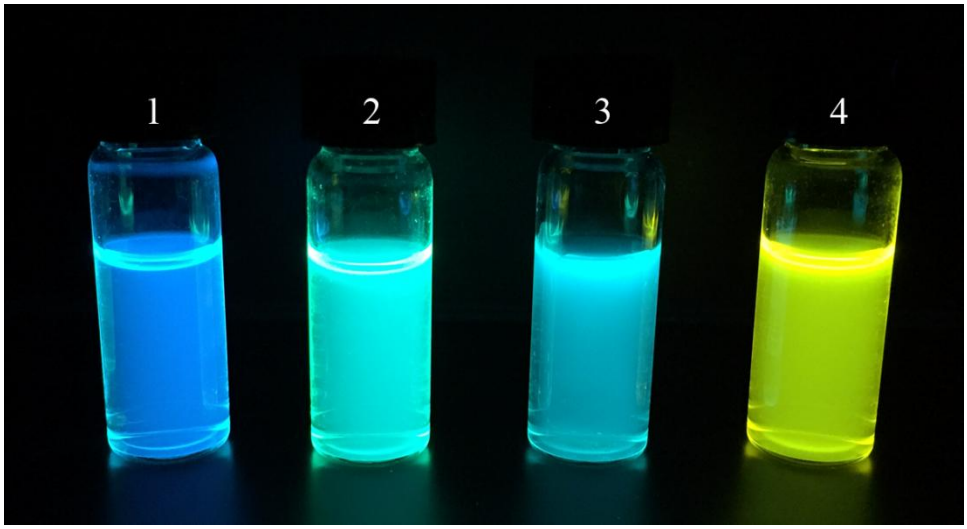


Figure 13. Pyrylium salts **1-4** in CH_3CN under UV lamp.

corresponding two perchlorates are reported to be 2.83 and 2.70 eV.[67] Their wavelengths of light emission were hypsochromically shifted in acetonitrile when compared with those of the corresponding perchlorate salts; and they showed Stokes shift of 46, 49, 53, and 66 nm, respectively. The wavelengths of light emission of the corresponding perchlorates are 466, 490, and 546 nm and their Stokes shifts are 61, 62 and 78 nm.[66] Each of the emission peaks showed a well defined narrow full-width at half-maximum (fwhm) value in the range of 54-70 nm, which is the indication of a single chromophore responsible for the fluorescence. The quantum yields (Φ_F) of the pyrylium salts **1-4** were determined against diphenylanthracene (Φ_F) in cyclohexane and were found to be in the range 27-56%. The salt **3** had the lowest quantum yield, as expected, due to heavy atom effect.[44] The corresponding perchlorate salts are reported to have 60-82%.[66] The optical properties of the pyrylium salts are greatly affected by chemical structure modifications with electron donating substituents in its primary chromophore, which is the cation. These results suggested that the optical properties of these pyrylium salts can be tuned with the variation of organic counterions such as tosylate. Furthermore, the quantum yields of pyrylium

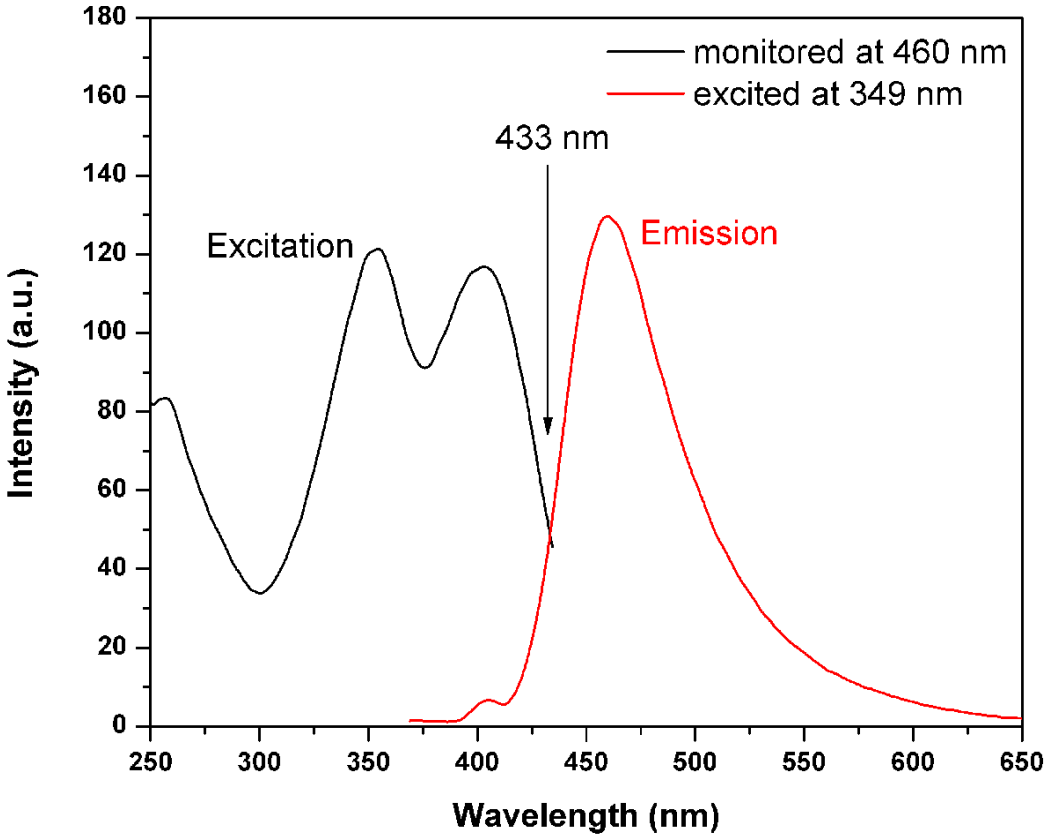


Figure 14. Emission spectrum of the pyrylium salt **1** recorded in polystyrene film cast from $CHCl_3$.

tosylates were found to be lower than those of pyrylium perchlorates, which are in excellent agreement with the results of photoluminescent ionic liquid crystals.[50]

The light emission in the solid states of **1-4** was too weak to detect presumably due to aggregation induced self-quenching. However, by introducing these salts in inert polystyrene matrices, their light emission was measured and found to be significantly enhanced and, therefore, we were able to assess their optical properties in the solid states. For example, the fluorescence spectrum of **1** in thin film cast from polystyrene matrix from chloroform is displayed in Figure 14. It exhibited λ_{em} peak at 460 nm when excited at 349 nm of light, which is bathochromically shifted by 10 nm when compared with that of solution spectrum. This result

suggested that light emission occurred from single molecules of **1** in this inert matrix what known as dilution effect.[41,68-71]

CHAPTER 4

CONCLUSIONS

This study described versatile synthetic methods of synthesis for a series of 2,4,6-triarylpyrylium tosylate salts via dehydrocyclization reaction by using *p*-toluenesulfonic acid, which provides significantly safe reaction condition than the conventional acid catalysts mentioned earlier. The chemical structures were fully characterized by ^{1}H, and ^{13}C NMR spectroscopy techniques and elemental analysis. The overall percent yields of these methods were comparable to those previously reported in the literature.[12-15] They have good solubility in various common organic solvents, and their thermal stabilities were at the temperature around 300 ℃. Given the organic salts, their thermal stabilities are considered to be excellent. Additionally, one of the pyrylium salts showed amorphous property based on DSC analyses. Due to the presence of chromophores, they exhibited photoluminescence properties in solution, and their light emission was as low as in the blue range and as high as the green spectrum of light depending on the substituents containing in the phenyl rings of the pyrylium ring. Although they did not emit light in the solid states due to aggregation induced self-quenching; however, they did emit light from inert polystyrene matrices. The optical properties of pyrylium salts were dependent on the chemical structures of not only cations but also anions. Their properties can be further tuned by structural modification to suit their multitude applications.

The future work of this project would involve further structural modifications with different substituents patterns including electron withdrawing moieties. Time-resolved fluorescence lifetime measurement would provide a better understanding of these materials.

Additionally, the pyrylium salts can be transformed into various heterocyclic molecules. Especially, pyridinium salts can be conveniently prepared via ring-transmutation and metathesis reactions by using aliphatic or aromatic primary amines. The literature contains many examples of pyridinium salts that exhibit amorphous, ionic liquid, and ionic liquid crystal properties.[72]

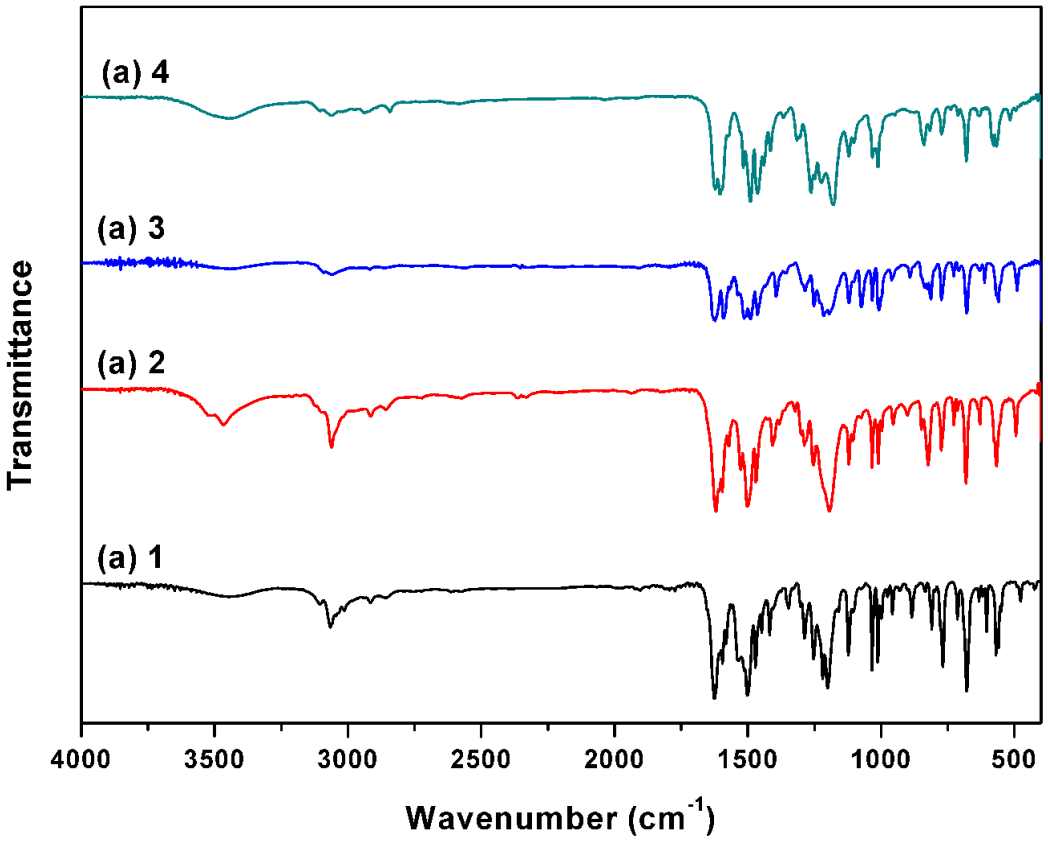


Figure S1. FTIR spectra of the pyrylium salts **1**-**4** taken at room temperature.

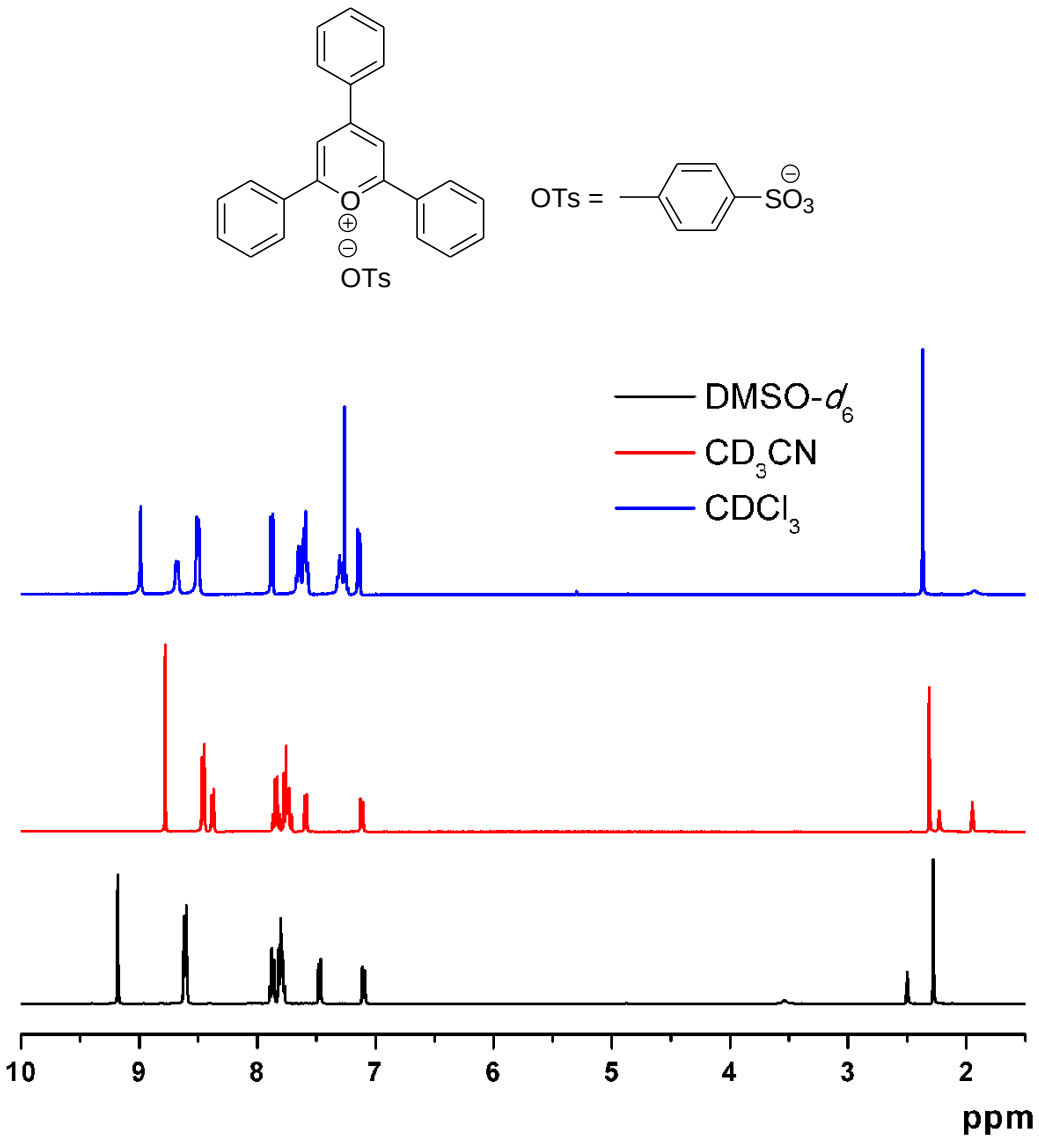


Figure S2. ^{1}H NMR spectra of the pyrylium salt **1** in DMSO-d_6, CD_3CN, and $CDCl_3$ recorded at room temperature.

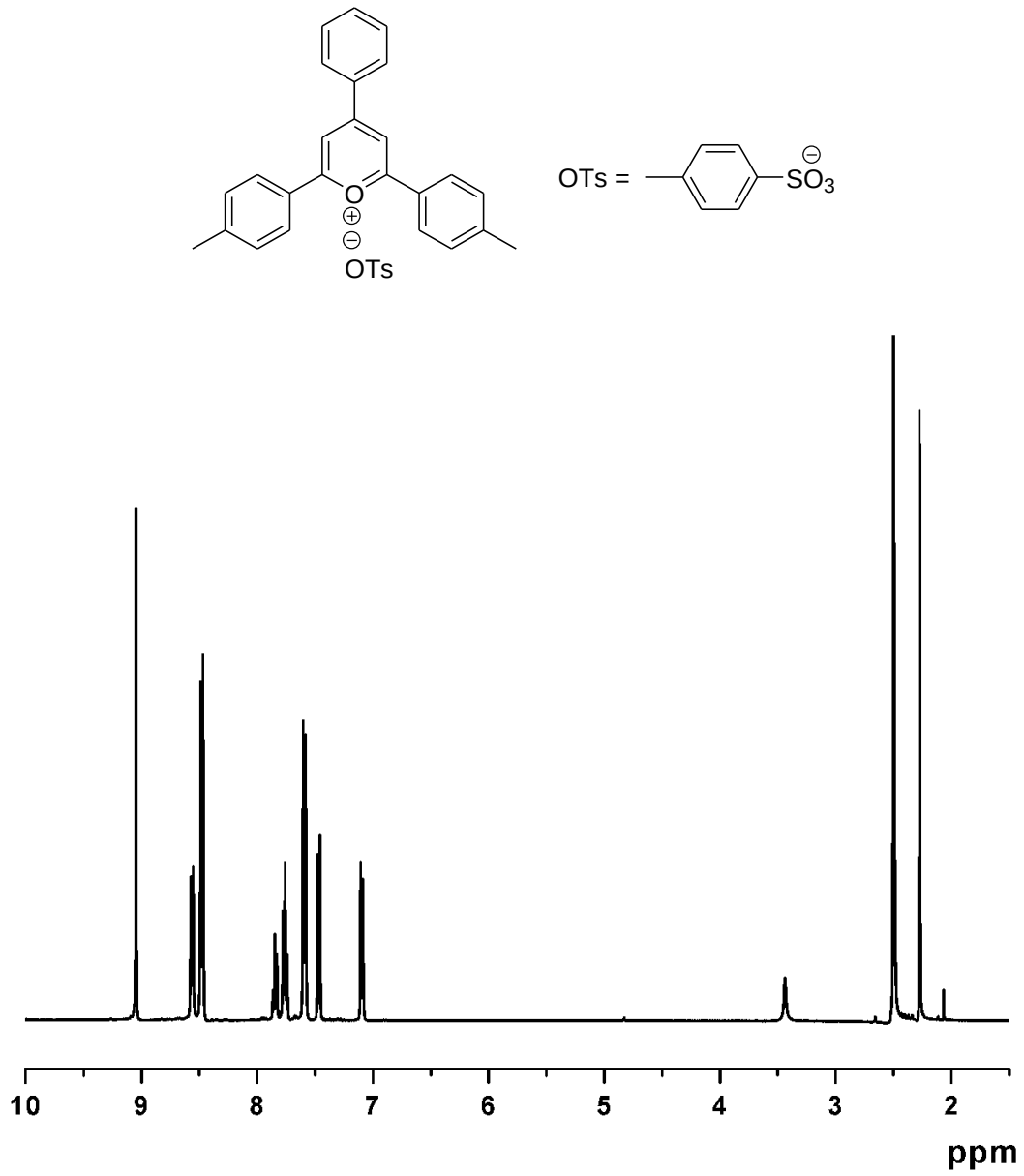


Figure S3. ^{1}H NMR spectrum of the pyrylium salt **2** in DMSO-d_6 recorded at room temperature.

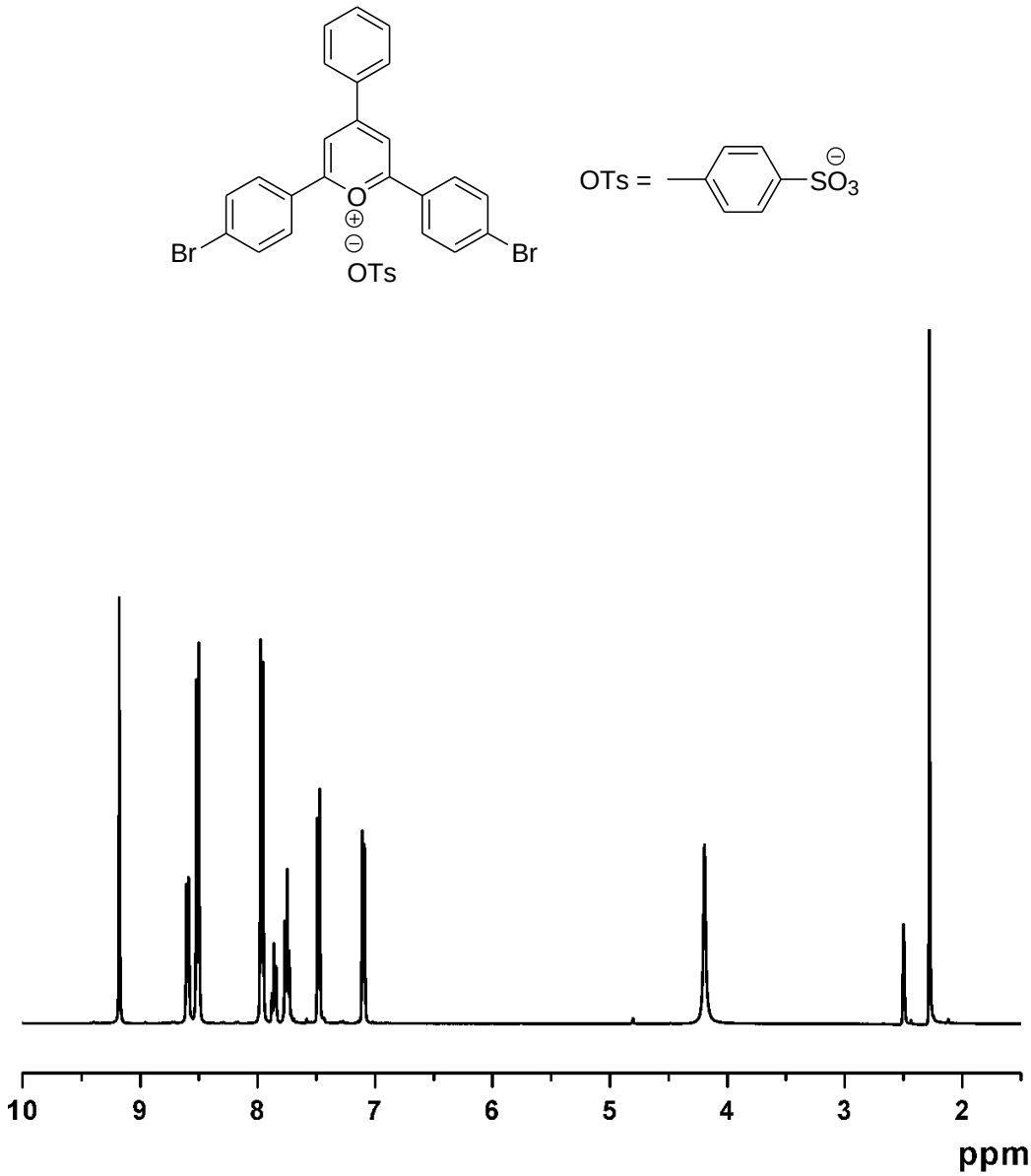


Figure S4. ^{1}H NMR spectrum of the pyrylium salt **3** in DMSO-d_6 recorded at room temperature.

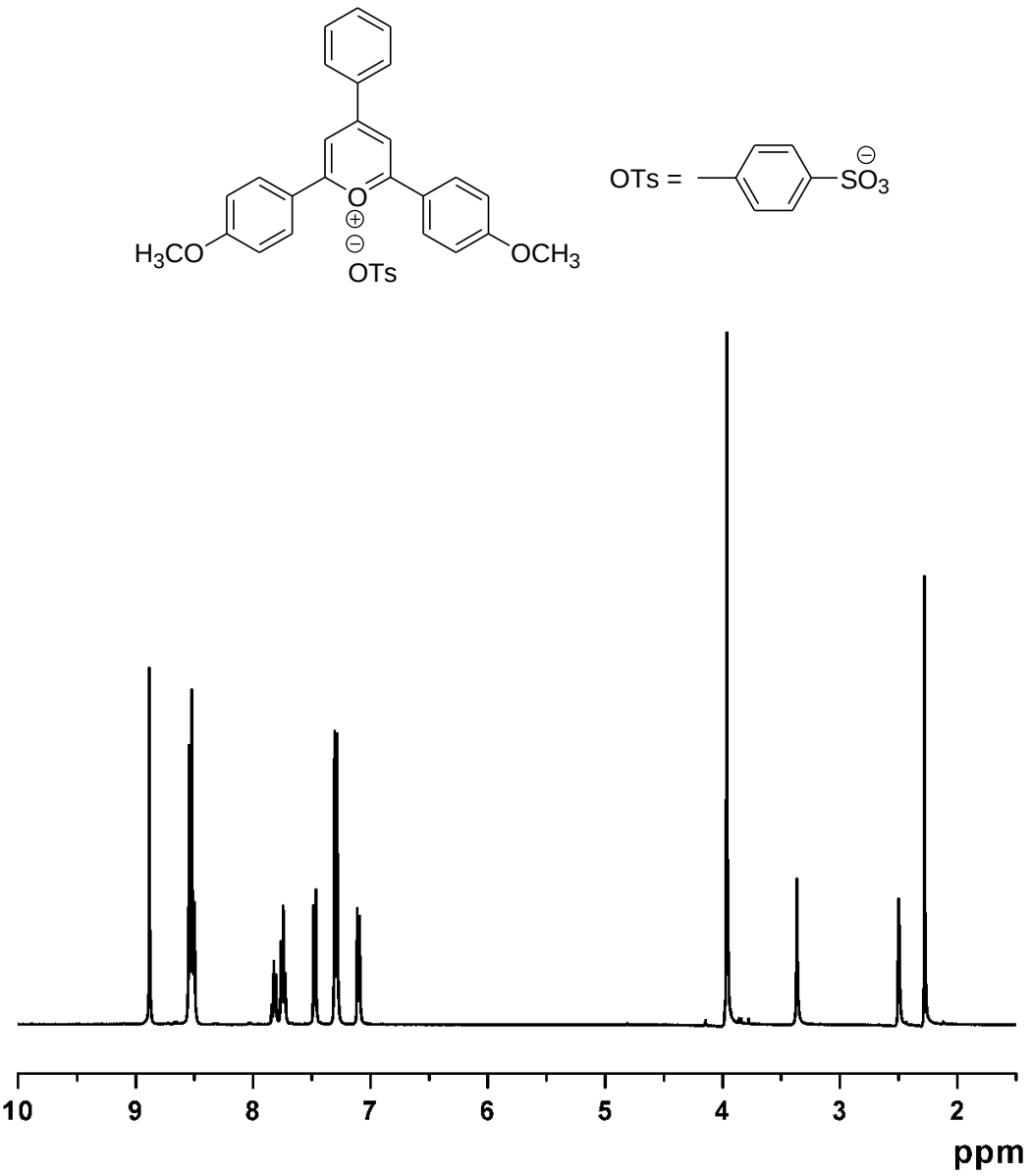


Figure S5. ^{1}H NMR spectrum of the pyrylium salt **4** in DMSO-d_6 recorded at room temperature.

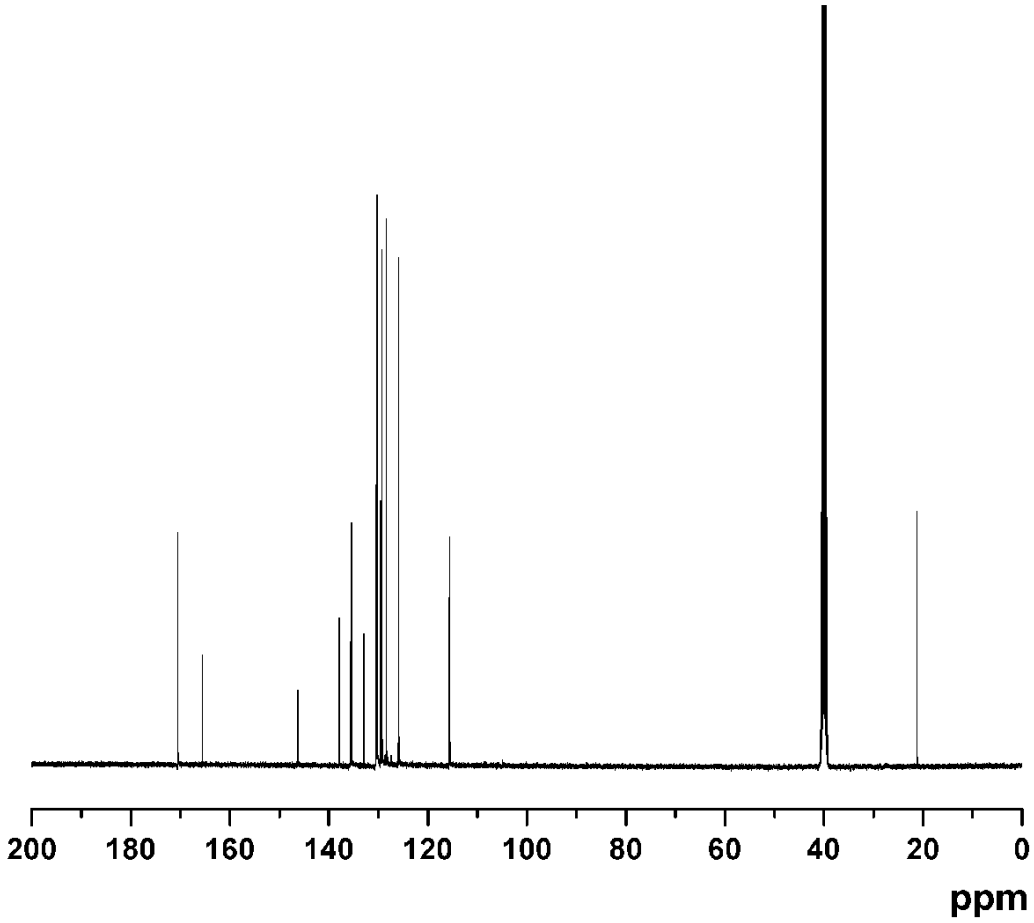


Figure S6. ^{13}C NMR spectrum of the pyrylium salt **1** in DMSO-d_6 recorded at room temperature.

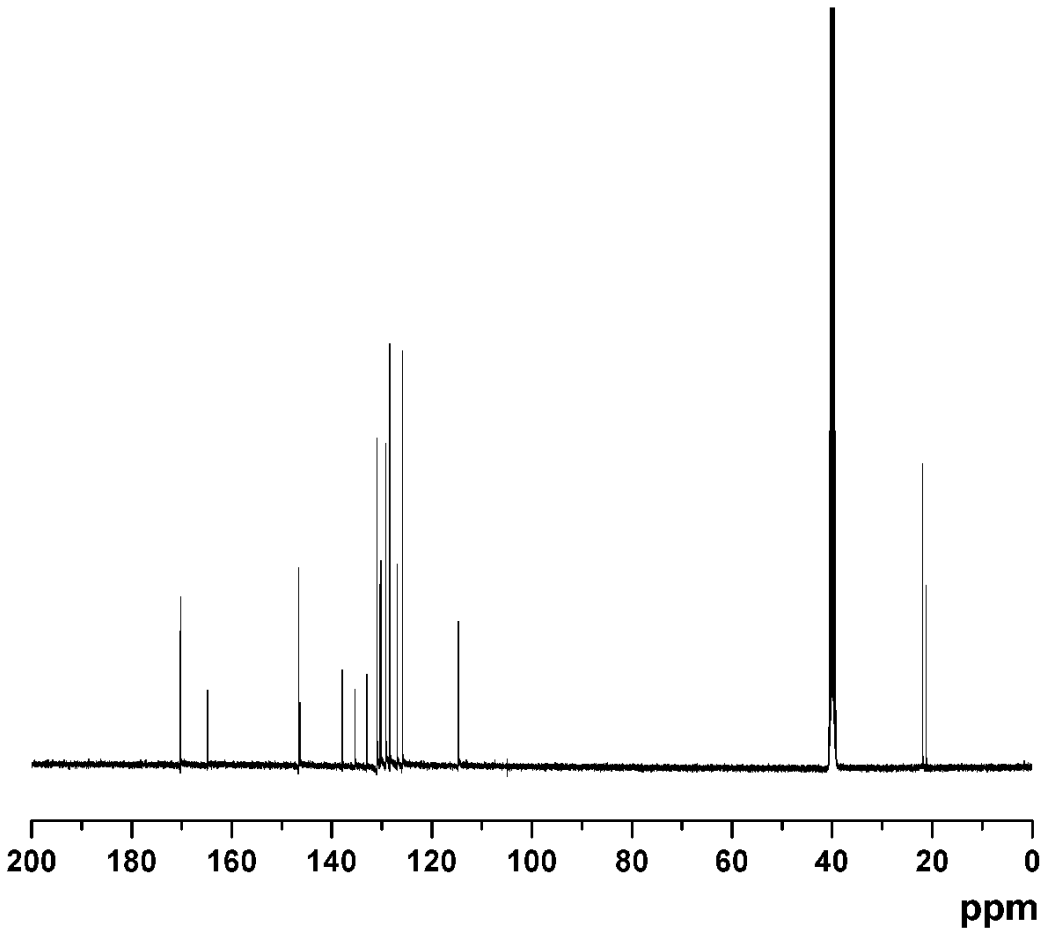


Figure S7. ^{13}C NMR spectrum of the pyrylium salt **2** in DMSO-d_6 recorded at room temperature.

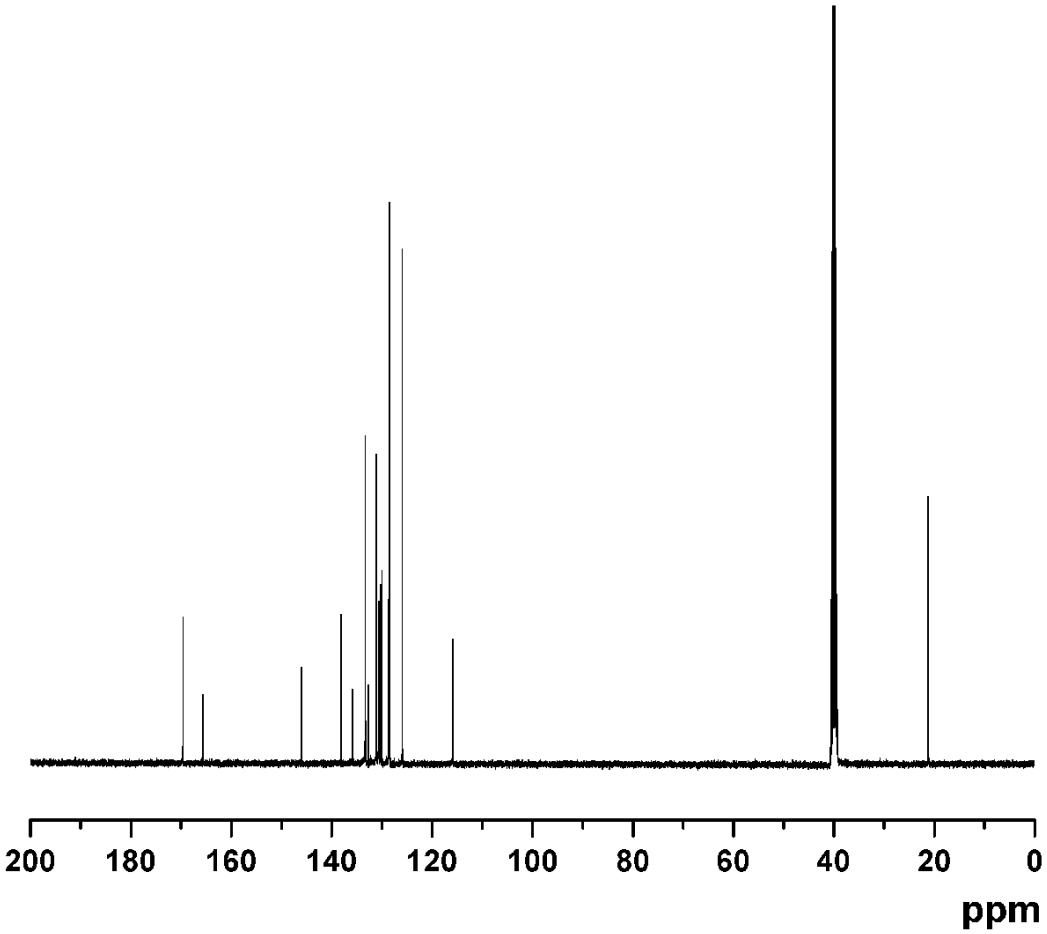


Figure S8. ^{13}C NMR spectrum of the pyrylium salt **3** in DMSO-d_6 recorded at room temperature.

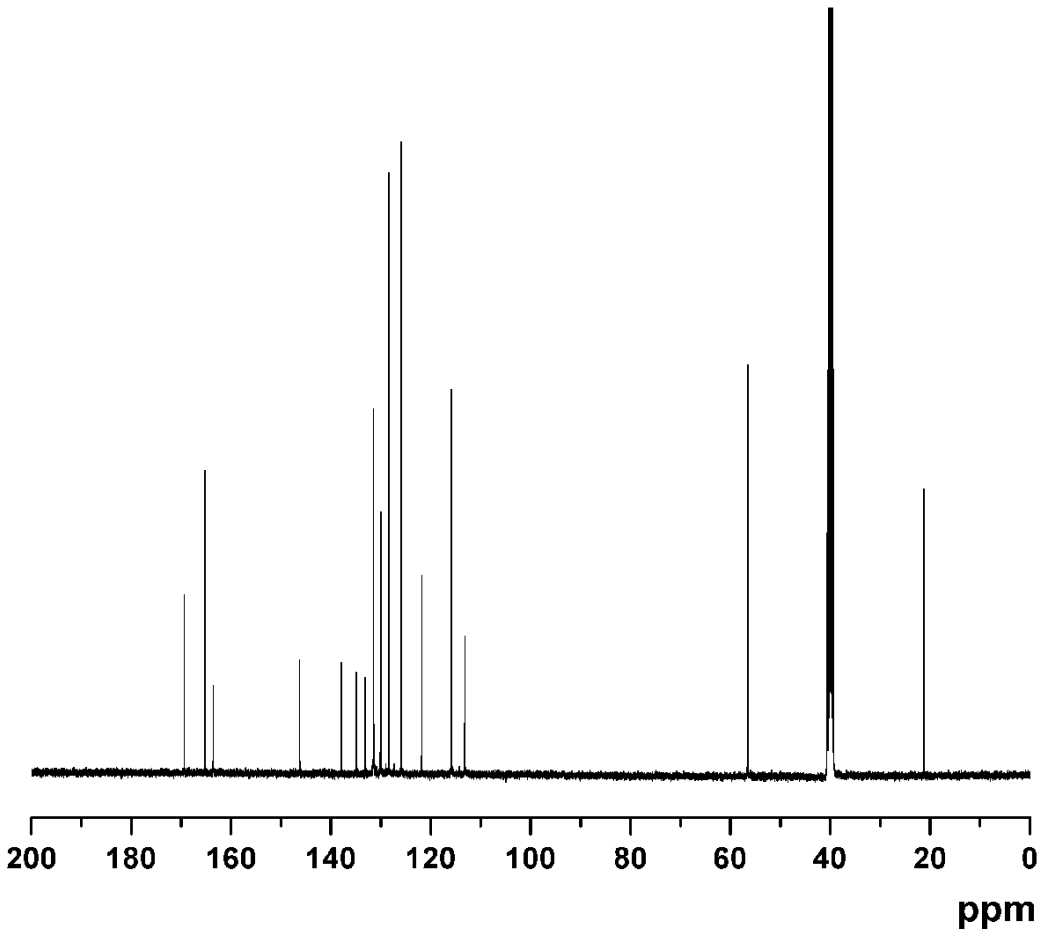


Figure S9. ^{13}C NMR spectrum of the pyrylium salt **4** in DMSO-d_6 recorded at room temperature.

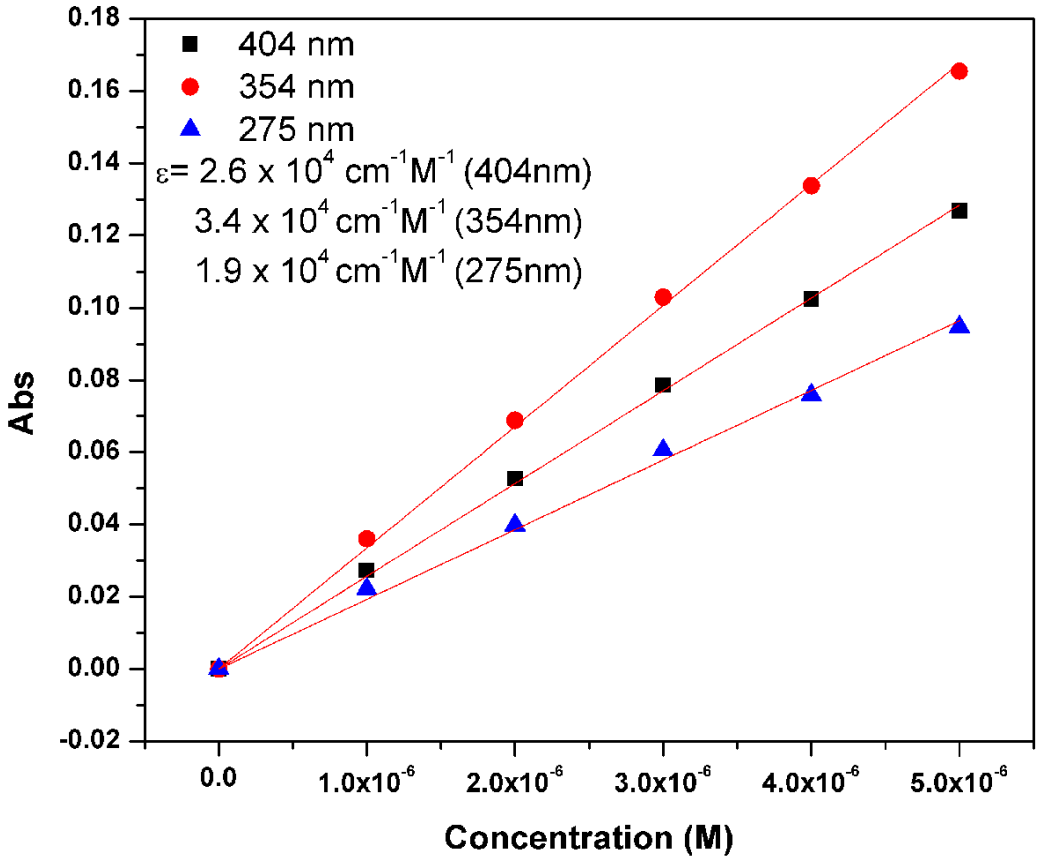


Figure S10. Beer's law plot of the pyrylium salt **1** in CH_3CN.

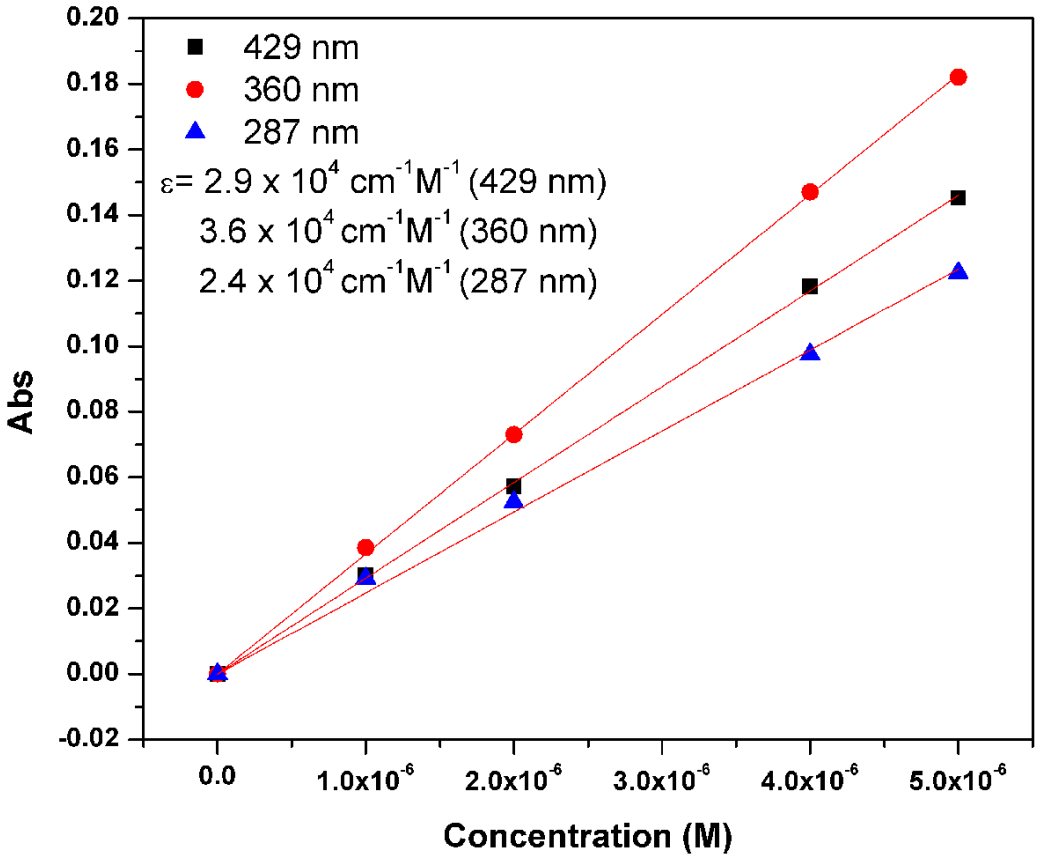


Figure S11. Beer's law plot of the pyrylium salt **2** in CH_3CN.

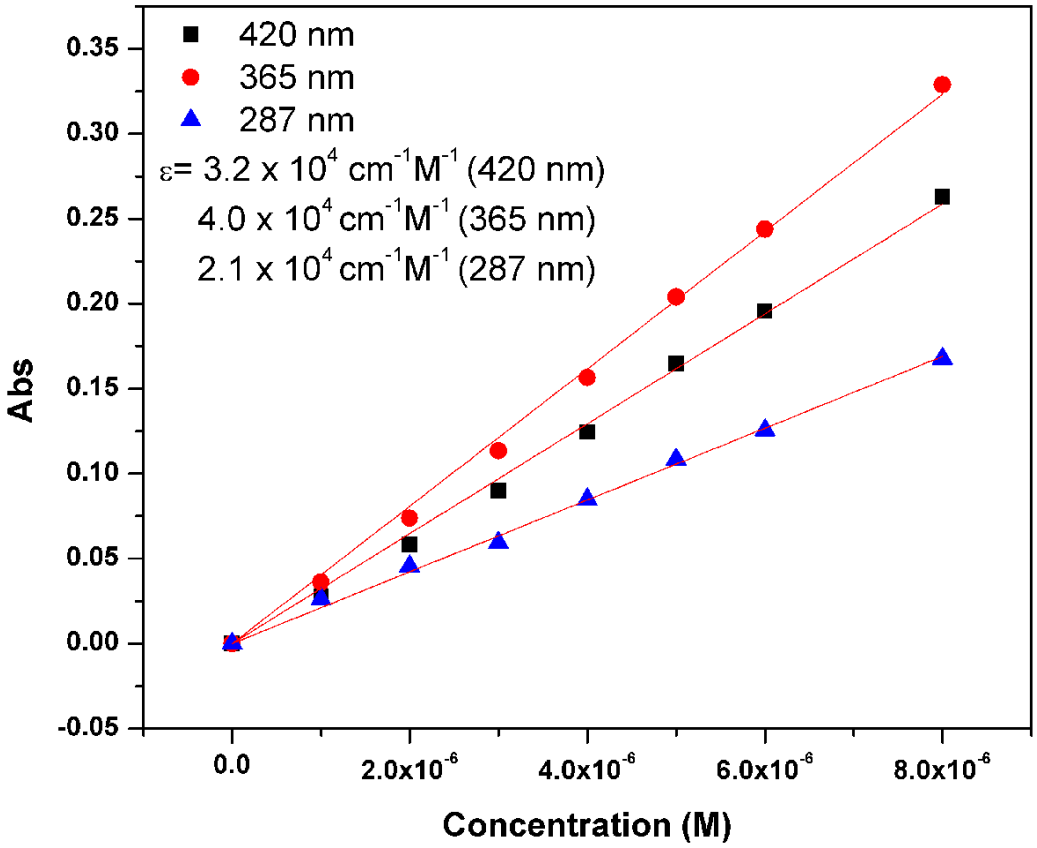


Figure S12. Beer's law plot of the pyrylium salt **3** in CH_3CN.

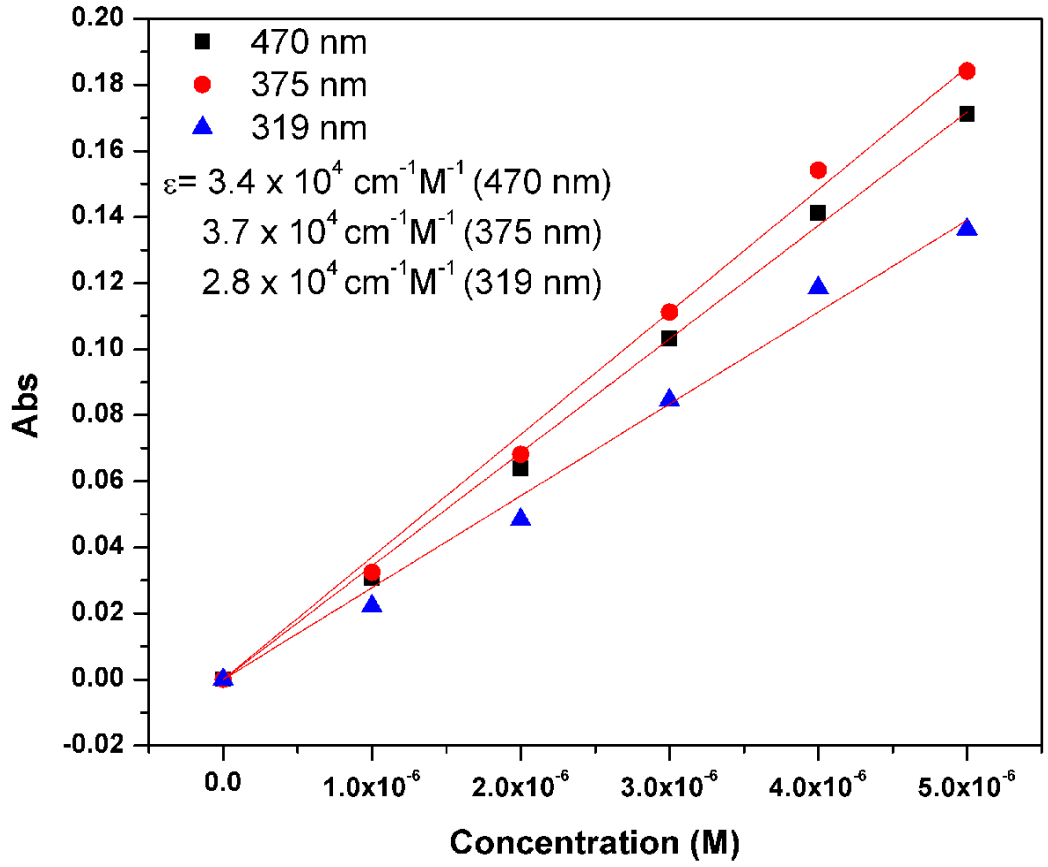


Figure S13. Beer's law plot of the pyrylium salt **4** in CH_3CN.

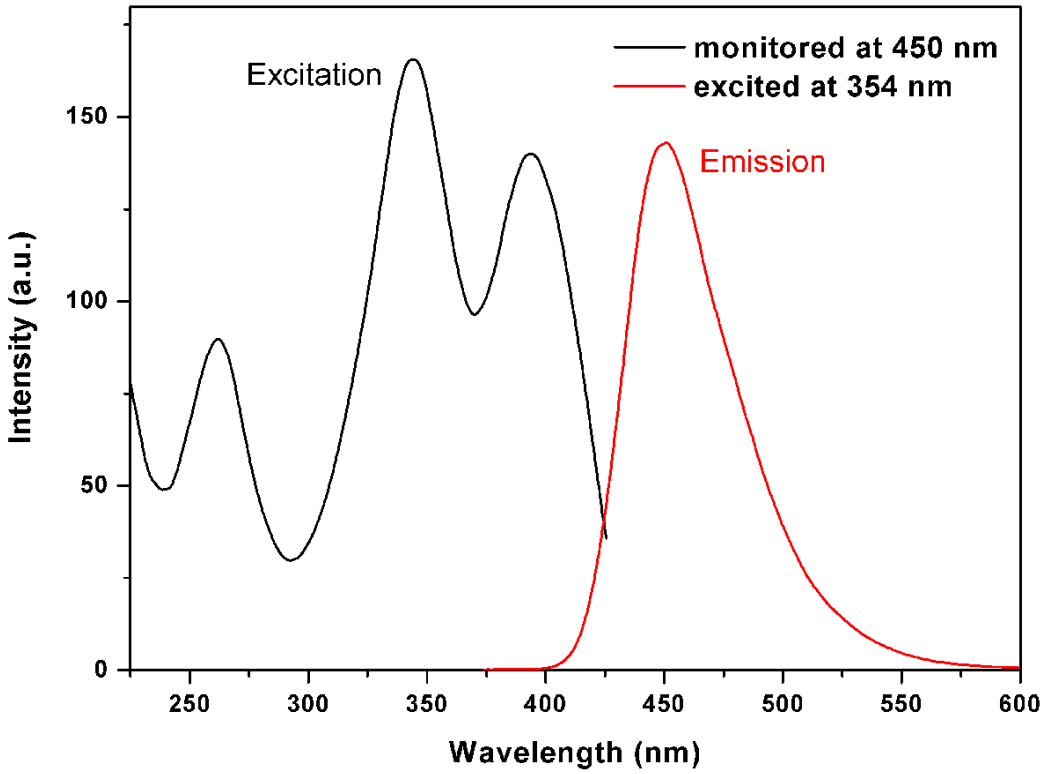


Figure S14. Excitation and emission spectra of the pyrylium salt **1** in CH_3CN recorded at room temperature.

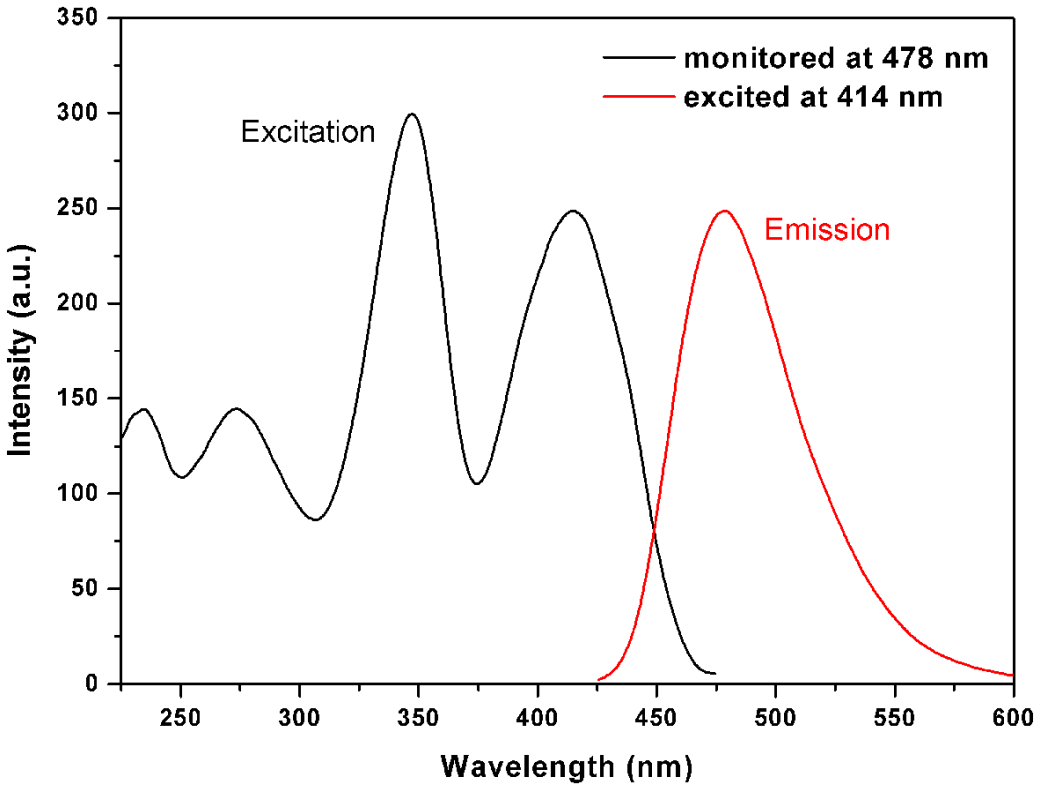


Figure S15. Excitation and emission spectra of the pyrylium salt **2** in CH_3CN recorded at room temperature.

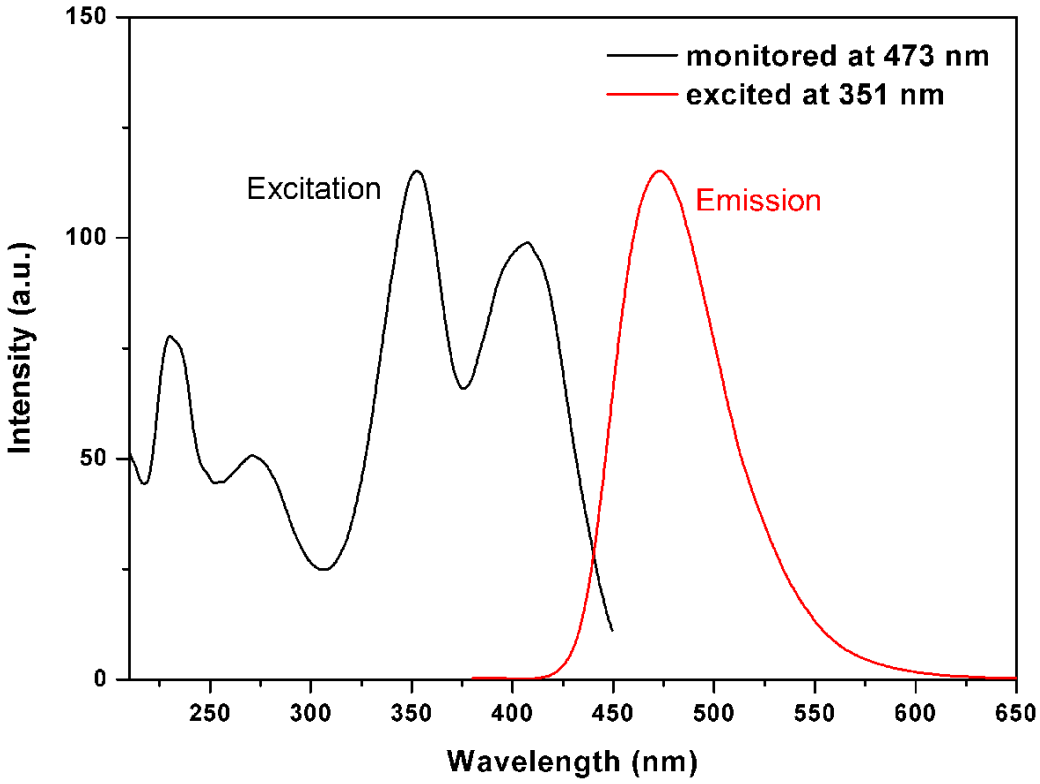


Figure S16. Excitation and emission spectra of the pyrylium salt **3** in CH_3CN recorded at room temperature.

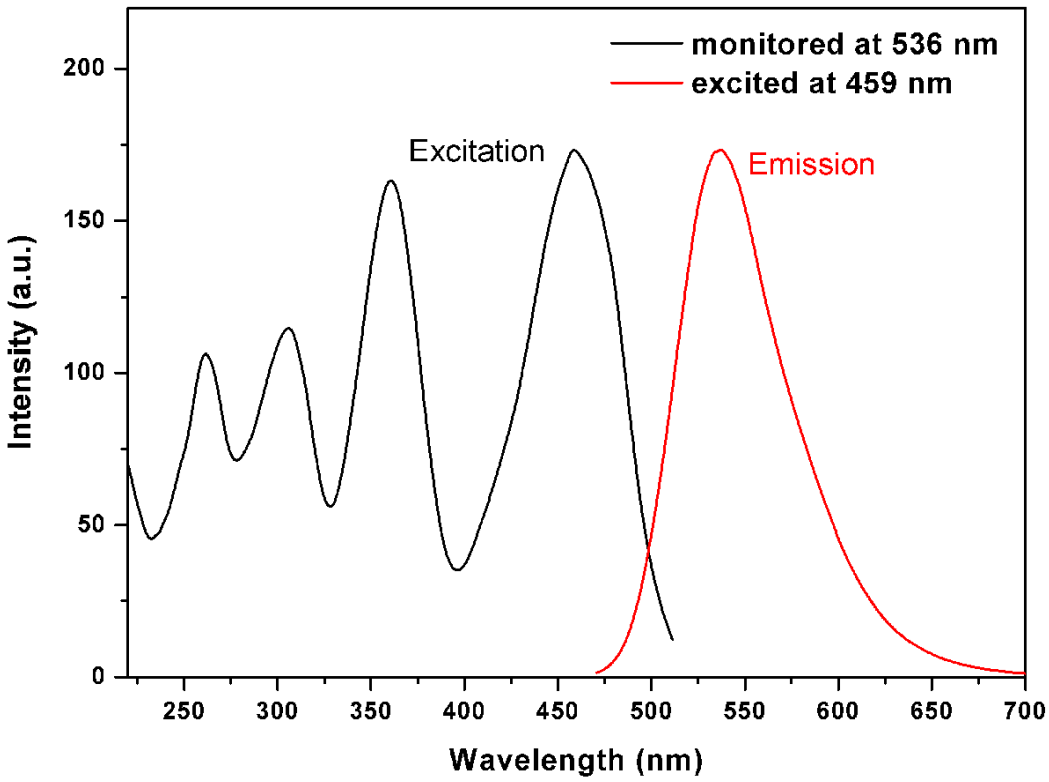


Figure S17. Excitation and emission spectra of the pyrylium salt **4** in CH_3CN recorded at room temperature.

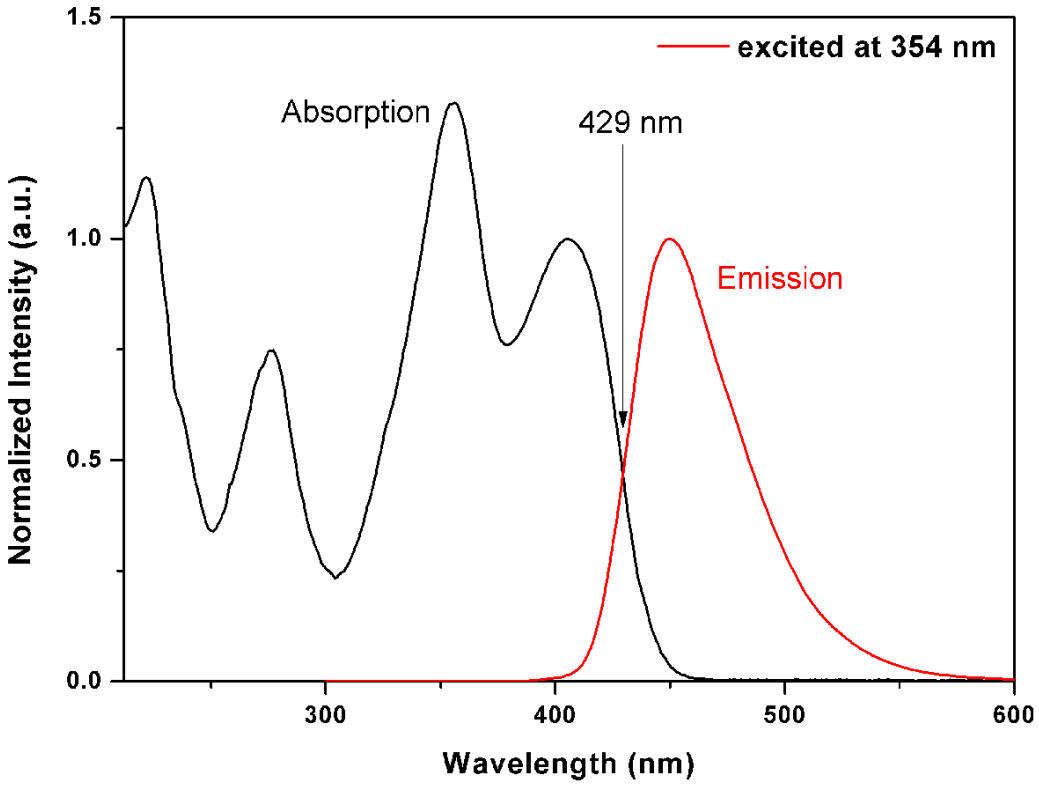


Figure S18. Absorption and emission spectra of the pyrylium salt **1** in CH_3CN recorded at room temperature.

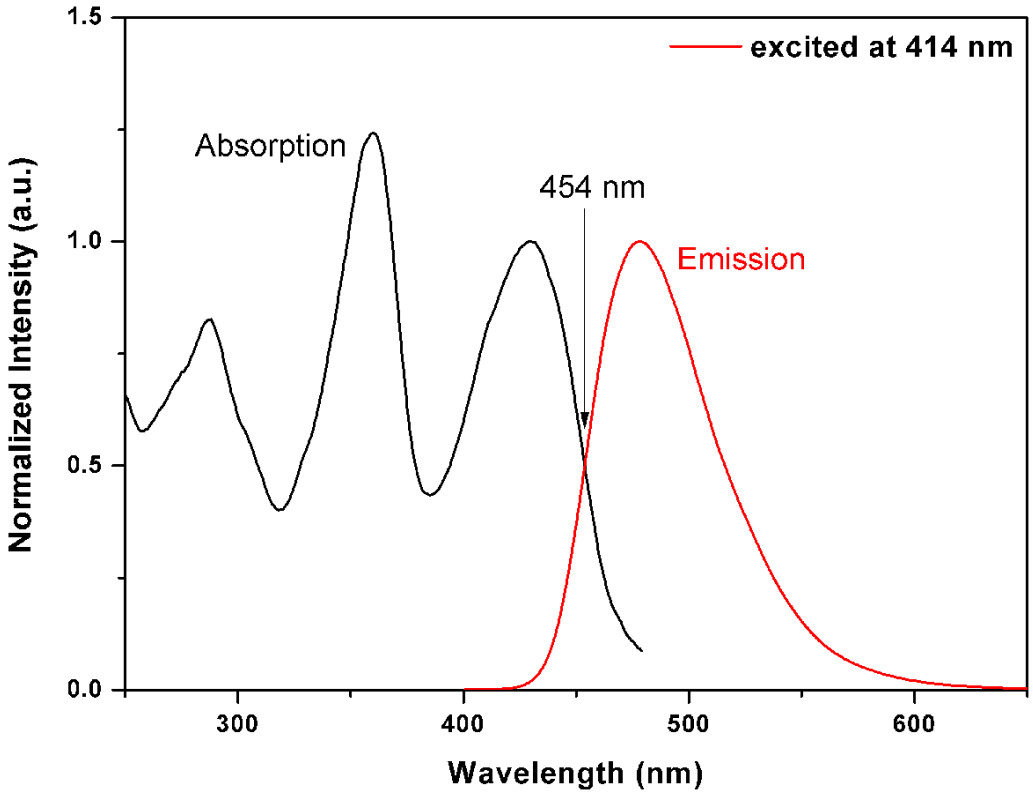


Figure S19. Absorption and emission spectra of the pyrylium salt **2** in CH_3CN recorded at room temperature.

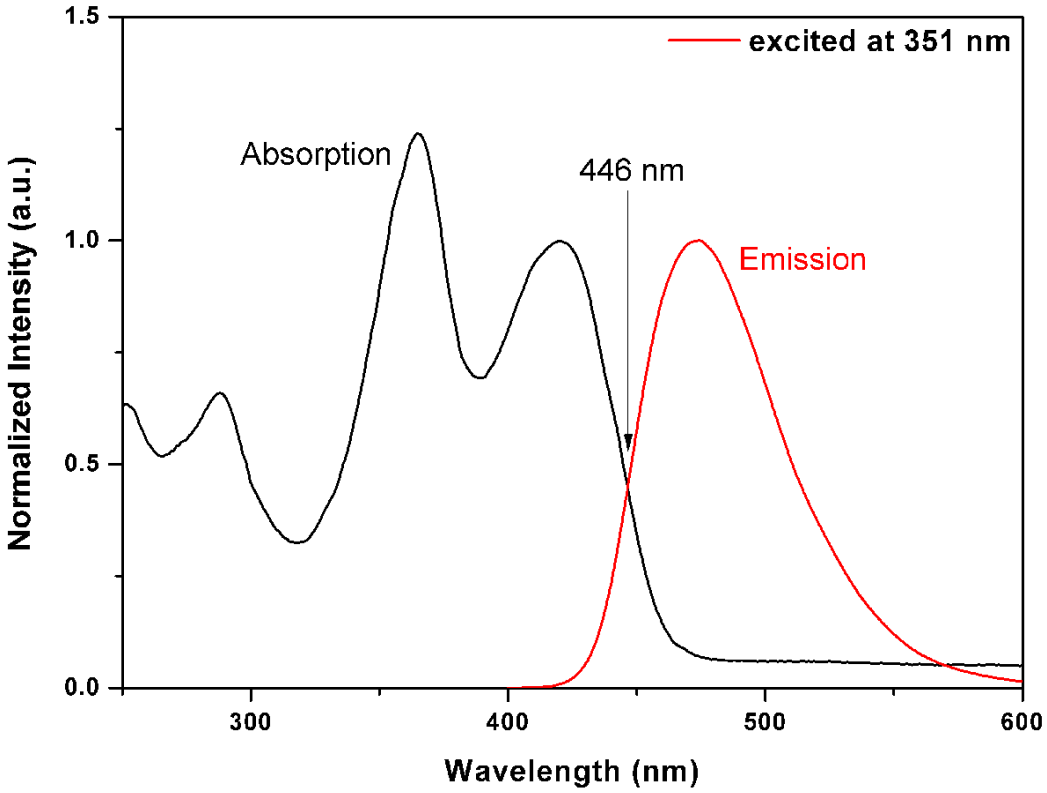


Figure S20. Absorption and emission spectra of the pyrylium salt **3** in CH_3CN recorded at room temperature.

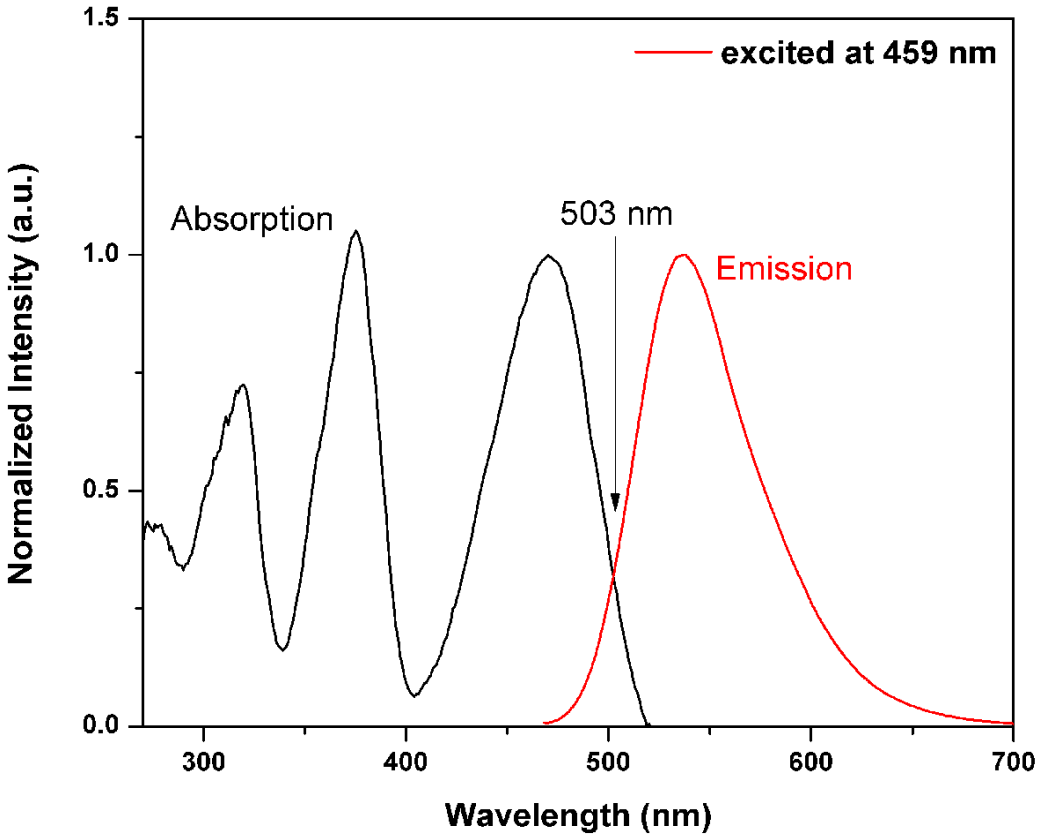


Figure S21. Absorption and emission spectra of the pyrylium salt **4** in CH_3CN recorded at room temperature.

REFERENCES

1. Balaban, A. T. Aromaticity of Six-Membered Rings with One Heteroatom. In *Aromaticity in Heterocyclic Compounds*; Krygowski, T. M., Cyranski, M. K., Eds.; Topics in Heterocyclic Chemistry; Springer-Verlag: Berlin, 2009; Vol. 19, pp 203-246.

2. Balaban T. S.; Balaban A. T. Six-Membered Hetarenes with One Chalcogen. In Science of Synthesis; Thomas, E. J., Ed.; Georg ThiemeVerlag: Stuttgart, 2003; Vol. 14, pp 11-200.

3. Baeyer, A.; Piccard, J. *Justus Liebigs Ann. Chem*. **1911**, *384*, 208.

4. Mouradzadegun, A.; Abadast, F. *Synlett*. **2014**, 448.

5. Bello, A. M.; Kotra, L. P. *Tetrahedron Lett.* **2003**, *44*, 9271.

6. Balaban, A. T.; Schroth, W.; Fischer, G.W. *Adv. Heterocyl. Chem*. **1969**, *10*, 241.

7. Katritzky, A. R.; Brownlee, R. T. C.; Musumarra, G. *Heterocycles* **1979**, *12*, 775.

8. Baeyer, A.; Piccard, J. *Justus Liebigs Ann. Chem*. **1914**, *407*, 332.

9. Dilthey, W. *J. Prakt. Chem*. **1916**, *94*, 53.

10. Spitzner, R.; Radeglia, R.; Schroth, W. *Tetrahedron Lett*. **1985**, *26*, 3967.

11. Dilthey, W. *Ber. Dtsch. Chem. Ges*. **1919**, *52*, 1195.

12. Dorofeenko, G. N.; Krivun, S. V. *Zh. Obshch. Khim*. **1964**, *34*, 105.

13. Wizinger, R.; Losinger, S.; Ulrich, P. *Helv. Chim. Acta*. **1956**, *39*, 5.

14. Lombard, R.; Stéphan, *J-P, Bull. Soc. Chim.Fr*. **1958**, 1458.

15. Csürös, Z.; Deak, G.; Sallay, P. *ActaChim. Acad. Sci. Hung*. **1971**, *70*, 123.

16. Johnston, W. E.; Lèvre, R. J. W. *J. Chem. Soc*. **1932**, 2900.

17. Schill, G.; Zollenkopf, H. *Justus Liebigs Ann. Chem*. **1969**, *721*, 53.

18. Balaban, A. T. C. R. *Acad. Sci*. **1963**, *256*, 4242.

19. Dimroth, K.; Berndt, A.; Reichardt, C. *Org. Synth. Coll. Vol. V*. **1973**. 1128.

20. Dinculescu, A.; Balaban, A. T. *Org. Prep. Proced. Int*. **1984**, *16*, 407.

21. Amoros-Martic, L.; Carlin, R. B. *J. Am. Chem. Soc*. **1959**, *81*, 733.

22. Dimroth, K.; Reichardt, C.; Siepmann, T.; Bohlmann, F. *Justus Liebigs Ann. Chem*. **1963**, *661*, 1.

23. Dilthey, W.; Radmacher, A. *J. Prakt. Chem*. **1925**, *111*, 153.

24. von Kostanecki, S.; Rossbach, G. *Ber. Dtsch. Chem. Ges*. **1896**, *29*, 1488.

25. von Kostanecki, S.; Rossbach, G. *Ber. Dtsch. Chem. Ges*. **1896**, *29*, 1493.

26. Mouradzadegun, A.; Abadast, F. *Tetrahedron Lett*. **2013**, *54*, 2641.

27. Razus, A. C.; Birzan, L.; Cristea, M.; Tecuceanu, V.; Hanganu, A.; Enache C. *J. Heterocycl. Chem*. **2011**, *48*, 1019.

28. (a) Nedeltchev, A. K.; Han, H.; Bhowmik, P. K. *J. Mater. Chem*. **2011**, *21*, 12717. (b) Jo, T. S.; Koh, J. J.; Han, H.; Bhowmik, P. K. *Mater. Chem. Phys*. **2013**, *139*, 901.

29. Machado, V. G.; Stock, R. I.; Reichardt, C. *Chem. Rev*. **2014**, *114*, 10429.

30. Álvaro, M.; Aprile, C.; Carbonell, E.; Ferrer, B.; García, H. *Eur. J. Org. Chem*. **2006**, 2644.

31. Spiliopoulos, I. K.; Mikroyannidis, J. A. *Macromolecules* **2002**, *32*, 7254.

32. Dilthey, W. *J. Prakt. Chem*. **1917**, *95*, 407.

33. Miranda, M. A.; García, H. *Chem. Rev*. **1994**, *94*, 1063.

34. Jha, P. C.; Luo, Y.; Polyzos, I.; Persephonis, P.; Ågren, H. *J. Chem. Phys*. **2009**, *130*, 174312.

35. Rao, B. A.; Lee, J-Y.; Son, Y-A. *Supramol. Chem*. **2014**, *27*, 191.

36. Beltrán, A.; Burguete, M. I.; Abánades, D. R.; Pérez-Sala, D.; Luis, S. V.; Galindo, F. *Chem. Commun*. **2014**, *50*, 3579.

37. Wetzl, B. K.; Yarmoluk, S. M.; Craig, D. B.; Wolfbeis, O. S. *Angew. Chem. Int. Ed*. **2004**, *43*, 5400.

38. Wuts, P. G. M.; Greene, T. W. *Greene's Protective Groups in Organic Synthesis*, 4th ed.; John Wiley & Sons, Inc.: Hoboken, NJ, 2007.

39. Gao, Q.; Bao, F-P.; Feng, X-J.; Pan, Y-M.; Wang, H-S.; Li, D-P. *ARKIVOC* **2013** (iii) 49.

40. Peng, C.; Wang, Y.; Liu, L.; Wang, H.; Zhao, J.; Zhu, Q. Eur. *J. Org. Chem*. **2010**, 818.

41. Bhowmik, P. K.; Nedeltchev, A. K.; Han, H.; Jo, T. S.; Koh, J. J.; Senthilkumar, L.; Umadevi, P. *J. Photochem. Photobiol., A* **2014**, *283*, 45.

42. Pan, Y-M.; Zheng, F-J.; Lin, H-X.; Zhan, Z-P. *J. Org. Chem*. **2009**, *74*, 3148.

43. Deng, K.; Huai, Q-Y.; Shen, Z-L.; Li, H-J.; Liu, C.; Wu, Y-C. *Org. Lett*. **2015**, *17*, 1743.

44. Sarker, A. M.; Kaneko, Y.; Lahti, P. M.; Karasz, F. E. *J. Phys. Chem. A***2003**, *107*, 6533.

45. Williams, A. T. R.; Winfield, S. A.; Miller, J. N. *Analyst* **1983**, *108*, 1067.

46. Dimroth, K.; Reichardt, C.; Vogel, K. *Org. Synth*. **1969**, *49*, 121.

47. Hirsch, S. S.; Bailey, W. J. *J. Org. Chem*. **1978**, *43*, 4090.

48. Moghimi, A. *J. Org. Chem*. **2002**, *67*, 2065.

49. Bello, A. M.; Kotra, L. P. *Tetrahedron Letters* **2003**, *44*, 9271.

50. Westphal, E.; da Silva, D. H.; Molin, F.; Gallardo, H. *RSC Adv*. **2013**, *3*, 6442.

51. Luo, S. C.; Sun, S.; Deorukhkar, A. R.; Lu, J. T.; Bhattacharyya, A.; Lin, I. J. B. *J. Mater. Chem.* **2011**, *21*, 1866.

52. Ye, Y.; Elabd, Y. A. *Polymer* **2011**, *52*, 1309.

53. Dobbs, W.; Douce, L.; Allouche, L.; Louati, A.; Malbosc, F.; Welter, R. *New J. Chem.* **2006**, *30*, 528.

54. Lin, S.-T.; Ding, M.-F.; Chang, C.-W.; Lue, S.-S. *Tetrahedron* **2004**, *60*, 9441.

55. Jo, T. S.; McCurdy, W. L.; Tanthmanatham, O.; Kim, T. K.; Han, H.; Bhowmik, P. K.; Heinrich, B.; Donnio, B. *J. Mol. Struct.* **2012**, *1019*, 174.

56. Cardinaels, T.; Lava, K.; Goossens, K.; Eliseeva, S. V.; Binnemans, K. *Langmuir* **2011**, *27*, 2036.

57. Bhowmik, P. K.; Han, H.; Nedeltchev, I. K.; Cebe, J. J.; Kang, S. W.; Kumar, S. *Liq. Cryst.* **2006**, *33*, 891.

58. Herstedt, M.; Henderson, W. A.; Smirnov, M.; Ducasse, L.; Servant, L.; Talaga, D.; Lassègues, J. C. *J. Mol. Struct.* **2006**, *783*, 145.

59. Roche, J. D.; Gordon, C. M.; Imrie, C. T.; Ingram, M. D.; Kennedy, A. R.; Celso, F. L.; Trilo, A. *Chem. Mater.* **2003**, *15*, 3089.

60. Tonzola, C. J.; Kulkarni, A. P.; Gifford, A. P.; Kaminsky, W.; Jenekhe, S. A. *Adv. Funct. Mater.* **2007**, *17*, 863.

61. Hancock, J. M.; Gifford, A. P.; Zhou, Y.; Lou, Y.; Jenekhe, S. A. *Chem. Mater.* **2006**, *18*, 4924.

62. Eaton, D. F. *Pure Appl. Chem.* **1988**, *60*, 1107.

63. Fery-Forgues, S.; Lavabre, D. *J. Chem. Edu.* **1999**, *76*, 1260.

64. Lakowicz, J. R. Principles in Fluorescence Spectroscopy; 3rd ed., Springer: New York, 2006; Chapter 1, pp1-26.

65. Christiano, R.; Eccher, J.; Bechtold, I. H.; Tironi, C. N.; Vieira, A. A.; Molin, F.; Gallardo, H. *Langmuir* **2012**, *28*, 11590.

66. Haucke, G.; Czerney, P.; Cebulla, F. *Ber. Bunsenges. Phys. Chem.* **1992**, *96*, 880.

67. Farid, S.; Dinnocenzo, J. P.; Merkel, P. B.; Young, R. H.; Shukla, D. *J. Am. Chem. Soc.* **2011**, *133*, 4791.

68. Huang, W. Y.; Yun, H.; Lin, H. S.;Kwei, T. K.; Okamoto, Y.*Macromolecules* **1999**, *32*, 8089.

69. He, G.; Li, Y.; Liu, J.; Yang, Y.*Applied Physics Letters* **2002**, *80*, 4247.

70. Bahirwar, B. M.;Atram, R. G.;Pode, R.B.; Moharil, S. V. *Mater. Chem. Phys.* **2007**, *106*, 364.

71. Raut, S. B.; Dhoble, S. J.; Atram, R. G. Synth. Met. **2011**, *161*, 391.

72. Binnemans, K. *Chem. Rev*. **2005**, *105*, 4148.

VITA

Graduate College
University of Nevada, Las Vegas

Jung Jae Koh

Degrees:

Bachelor of Science, Biochemistry, 2011
University of Nevada, Las Vegas

Honors and Awards:

1. Chemistry Department Outstanding Graduate Student Award (2015)
2. ACS Southern Nevada Chapter Annual Research Poster Competition (2nd place, 2014)
3. ACS Southern Nevada Chapter Annual Research Poster Competition (1st place, 2013)
4. Special Projects Graduate Research Assistant (2013)
5. Graduate and Professional Student Association (GPSA) Travel Grant (2013)
6. UNLV Alumni Association Faculty Award (2011)
7. UNLV Alumni Association Faculty Award (2010)
8. Outstanding Chemistry Student at the CSN by ACS(2009)

Publications:

Refereed Publications:

1. Pradip K. Bhowmik, Alexi K. Nedeltchev, Haesook Han, Tae Soo Jo, Jung Jae Koh.Photoactive amorphous molecular materials based on bisquinoline diamines and their synthesis by Friedländer condensation reaction. *J. Photochem. Photobiol., A***2014**, *283*, 45-55.
2. Tae Soo Jo, Jung Jae Koh, Haesook Han, and Pradip K. Bhowmik. Solution,thermal and optical properties of bis(pyridinium salt)s including ionic liquids. *Mater.Chem. Phys*.**2013**, *139*, 901-910.
3. Jung Jae Koh, Christina In-bok Lee, Mihaela A. Ciulei, Haesook Han, and Pradip K. Bhowmik. Versatile synthetic methods for photoluminescentpyryliumtosylates. Green Chemistry, in preparation.
4. Tae Soo Jo, Haesook Han, Jung Jae Koh, Jongwon Park, Bidyut Biswas, Pradip K. Bhowmik, and Millicent A. Firestone. Synthesis and characterization of poly(pyridinium salt)s containing 2,7-diamino- 9,9-dioctylfluorene moieties with various organic counterions exhibiting both lyotropic liquid-crystalline and light-emitting properties. Polym. Chem., in preparation.

Refereed Conference Proceedings:

1. Tae Soo Jo, Jung JaeKoh, Haesook Han, and Pradip K. Bhowmik. Synthesis and Characterization ofWater-Soluble Poly(pyridinium salt)s Derived from Aromatic Diamines. *Polym.Prepr., Am. Chem. Soc. Div. Polym. Chem.***2011,***52(2),* 351-352.
2. Tae Soo Jo, Jung JaeKoh, Haesook Han, Pradip K. Bhowmik, and Longzhou Ma. Dispersions of Single-Walled Carbon Nanotubes with Rigid-Rod Poly(pyridinium salt)s. *Polym. Prepr.,Am. Chem. Soc. Div. Polym. Chem.* **2011,***52(2),* 250-251.

Abstracts and Presentations:

1. Jung Jae Koh. Versatile Methods of Synthesis for Blue Light-Emitting Pyrylium Salts. ACS Southern Nevada Section Poster Competition (November, 2014)
2. Tae Soo Jo, Jung Jae Koh, Haesook Han, Jongwon Park, Bidyut Biswas, andPradip K. Bhowmik.Synthesis of poly(pyridinium salt)s containing fluorene moieties in the main-chain with various organic counterions. ACS Southern Nevada Section Poster Competition (November, 2013)
3. Tae Soo Jo, Jung Jae Koh, Alexi K. Nedeltchev, Haesook Han, Pradip K. Bhowmik,and Hari D. Mandal. Synthesis and characterization of poly(pyridinium salt)s containing dioxyethylene units in the main-chain and their sensing performance toward acids in organic solvents. Poster Presentations, American Association for the Advancement of Science, Pacific Division 94th Annual Meeting, Las Vegas, June 2013.
4. Tae Soo Jo, Jung Jae Koh, Haesook Han, Jongwon Park, Bidyut Biswas, andPradip K. Bhowmik.Synthesis of poly(pyridinium salt)s containing fluorene moieties in the main-chain with various organic counterions. Abstracts of Papers, 245th ACS National Meeting & Exposition, New Orleans, LA, United States, April7−11, 2013.
5. Tae Soo Jo, Jung Jae Koh, Haesook Han, Pradip K. Bhowmik, and Hari D. Mandal. Synthesis of poly(pyridinium salt)s containing heterocyclic pyridine and triphenylamine moieties in the main-chain and their solution, thermal and optical properties. Abstracts of Papers, 245th ACS National Meeting & Exposition, New Orleans, LA, United States, April 7−11, 2013.
6. Tae Soo Jo, Jung Jae Koh, Alexi K. Nedeltchev, Haesook Han, Pradip K. Bhowmik,and Hari D. Mandal. Synthesis and characterization of poly(pyridinium salt)s containing dioxyethylene units in the main-chain and their sensing performance toward acids in organic solvents. Abstracts of Papers, 245th ACS National Meeting &Exposition, New Orleans, LA, United States, April 7−11, 2013.
7. Tae Soo Jo, Jung Jae Koh, Haesook Han, Jongwon Park, Bidyut Biswas, andPradip K. Bhowmik.Synthesis of poly(pyridinium salt)s containing fluorene moieties in the main-chain with various organic counterions. Poster Presentations, UNLV's First Annual Stem Summit – January 15th, 2013.
8. Tae Soo Jo, Jung Jae Koh, Haesook Han, Jongwon Park, Bidyut Biswas, andPradip K. Bhowmik.Synthesis of poly(pyridinium salt)s containing fluorene moieties in the main-chain with various organic counterions. Poster Presentations, American Chemical Society (ACS) Southern Nevada Local Section Poster Competition – December 13th, 2012.

9. Tae Soo Jo, Jung Jae Koh, Haesook Han, and Pradip K. Bhowmik.Synthesis andCharacterizationofWater-soluble Poly(pyridinium salt)s Derived from AromaticDiamines.Abstracts of Papers,242nd ACS National Meeting & Exposition, Denver, CO, United States,Aug. 28−Sep.1, 2011,POLY-573.
10. Tae Soo Jo, Jung Jae Koh, Haesook Han, Longzhou Ma and Pradip K. Bhowmik.Dispersionsof Single-Walled Carbon Nanotubes with Rigid-Rod Poly(pyridinium salt)s. Abstracts of Papers,242nd ACS National Meeting & Exposition, Denver, CO, United States, Aug. 28−Sep.1, 2011,POLY-97.

Thesis Title:

Versatile Synthetic Methods for Photoluminescent Pyrylium Tosylates

Thesis Examination Committee:

Chair, Pradip K. Bhowmik, Ph.D.
Committee Member, Vernon F. Hodge, Ph.D.
Committee Member, Dong-Chan Lee, Ph. D.
Graduate Faculty Representative, Laxmi P. Gewali, Ph.D.